Supporting Information For

Fluorescence of Cyclopropenium Ion Derivatives

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1.0 Quantum Yield Calculation

The quantum yield (ϕ), was measured relative to that of anthracene in ethanol.[1] Emission spectra for the quantum yield calculation were acquired using 1cm quartz cuvettes in a fluorescence spectrophotometer with a Xenon flash lamp at ambient temperature. Sample and standards were prepared as 1×10^{-5} M solutions in 95% ethanol. Entrance and exit slit widths were set to 5 mm, and the excitation wavelength was 334 nm for both the standard and sample, unless otherwise specified. Quantum yields were calculated using Equation S1, according to the 2011 IUPAC technical report on standards for photoluminescence quantum yield measurements in solution.[2]

$$\phi_f^x = \frac{F^x f_{st} n_x^2}{F^{st} f_x n_{st}^2} \phi_f^{st} \qquad \text{[Equation S1]}$$

Where ϕ_f^x and ϕ_f^{st} are the quantum yields of the sample and the standard, respectively. $F^x$and $F^{st}$are the integrated fluorescence intensities of sample and standard spectra. f_x and f_{st} are the absorption factors of the sample and standard at the excitation wavelength (where $f = 1 - 10^{-A}$, and A = absorbance). n_x and n_{st} are the refractive indices of the sample and reference solution, respectively, which were assumed to be the same in this experiment.

2.0 ^{1}H and ^{13}C NMR spectra of Derivatives and Intermediates.

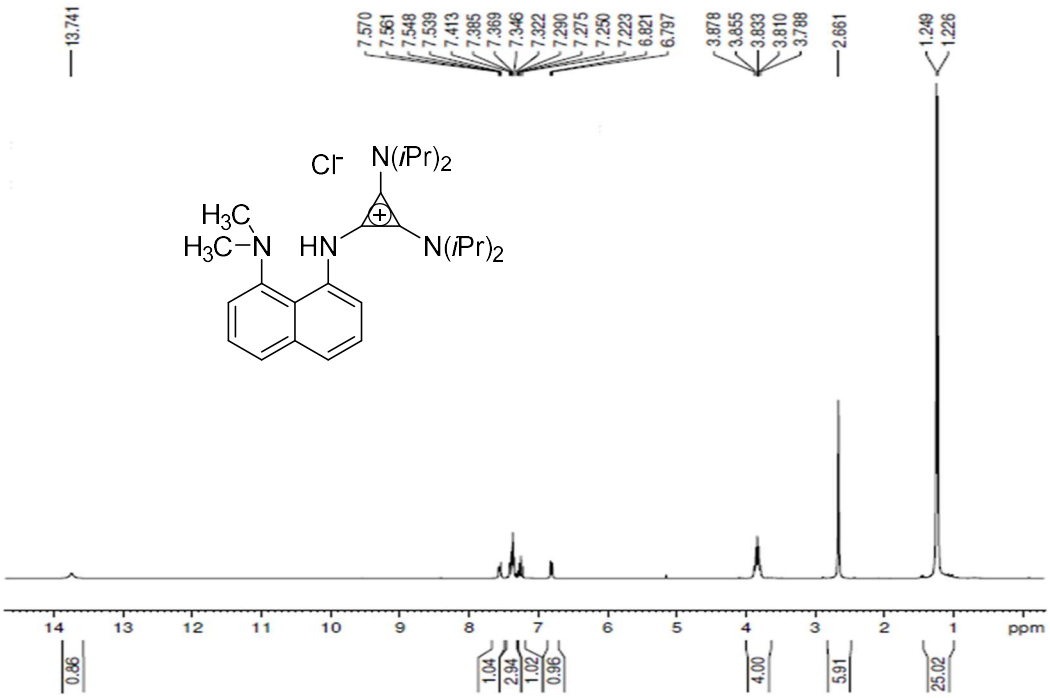

Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$.

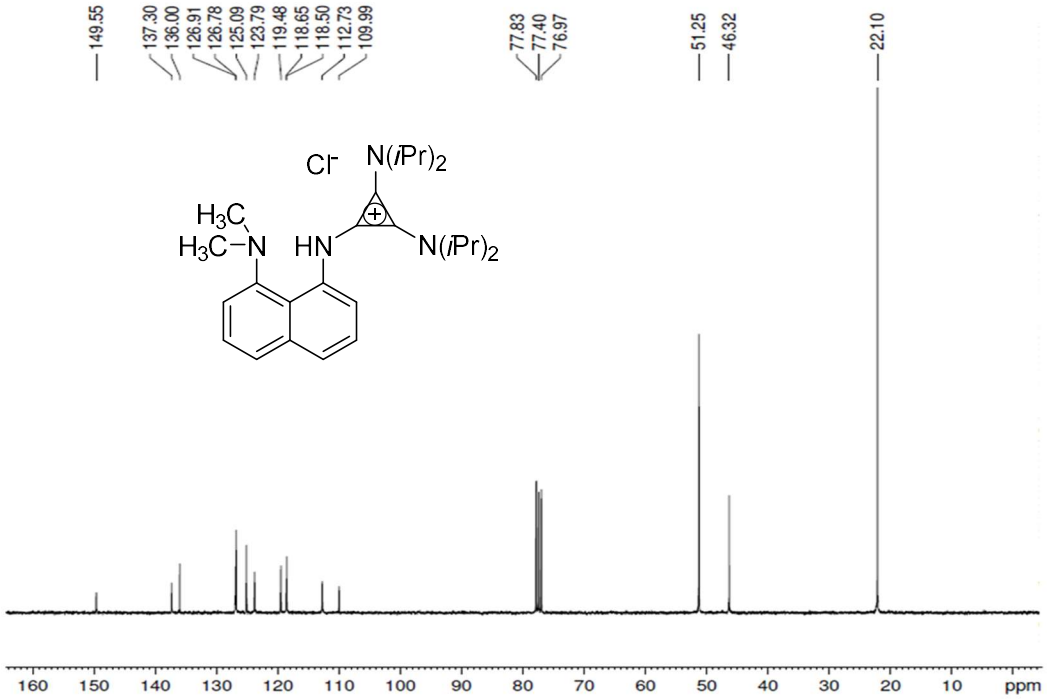

Figure S2. ^{13}C NMR spectrum of **1** in $CDCl_3$.

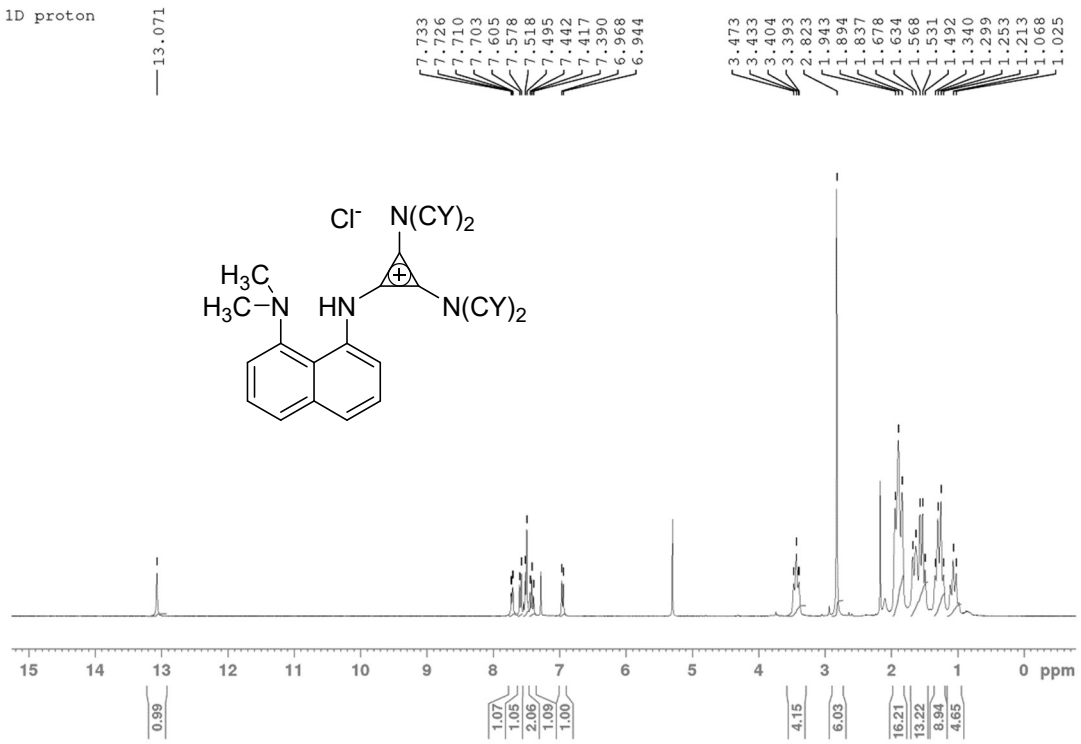

Figure S3. ^{1}H NMR spectrum of **6** in $CDCl_3$.

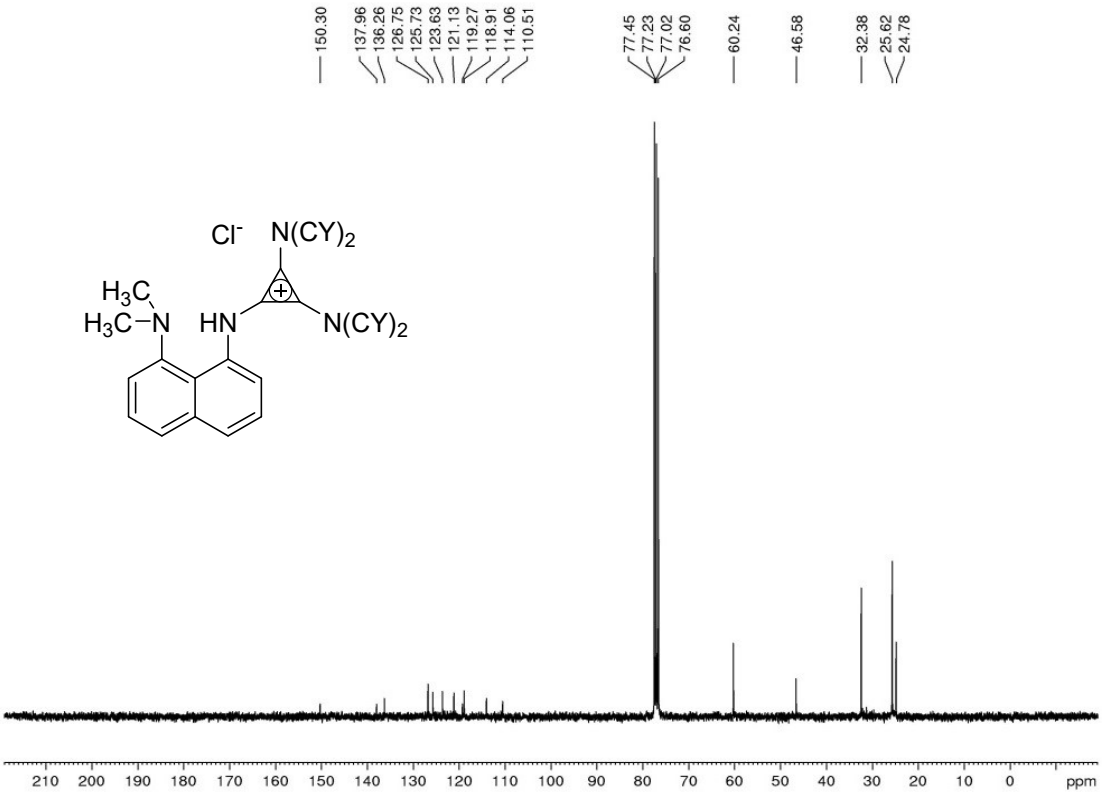

Figure S4. ^{13}C NMR spectrum of **6** in $CDCl_3$.

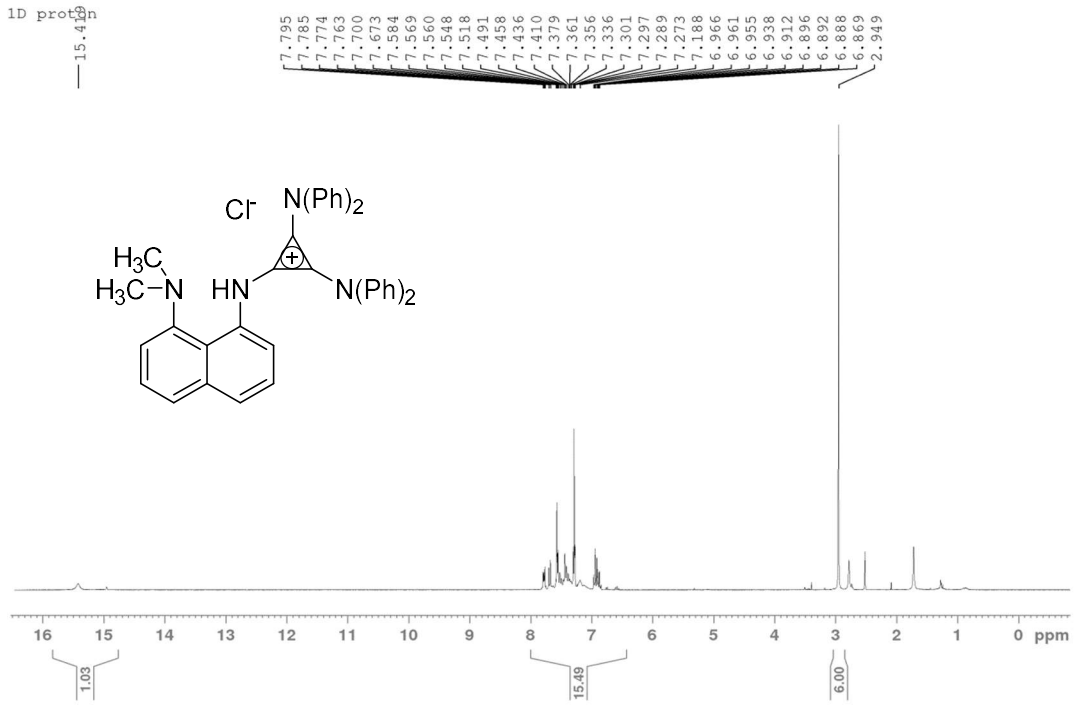

Figure S5. ^{1}H NMR spectrum of **7** in $CDCl_3$.

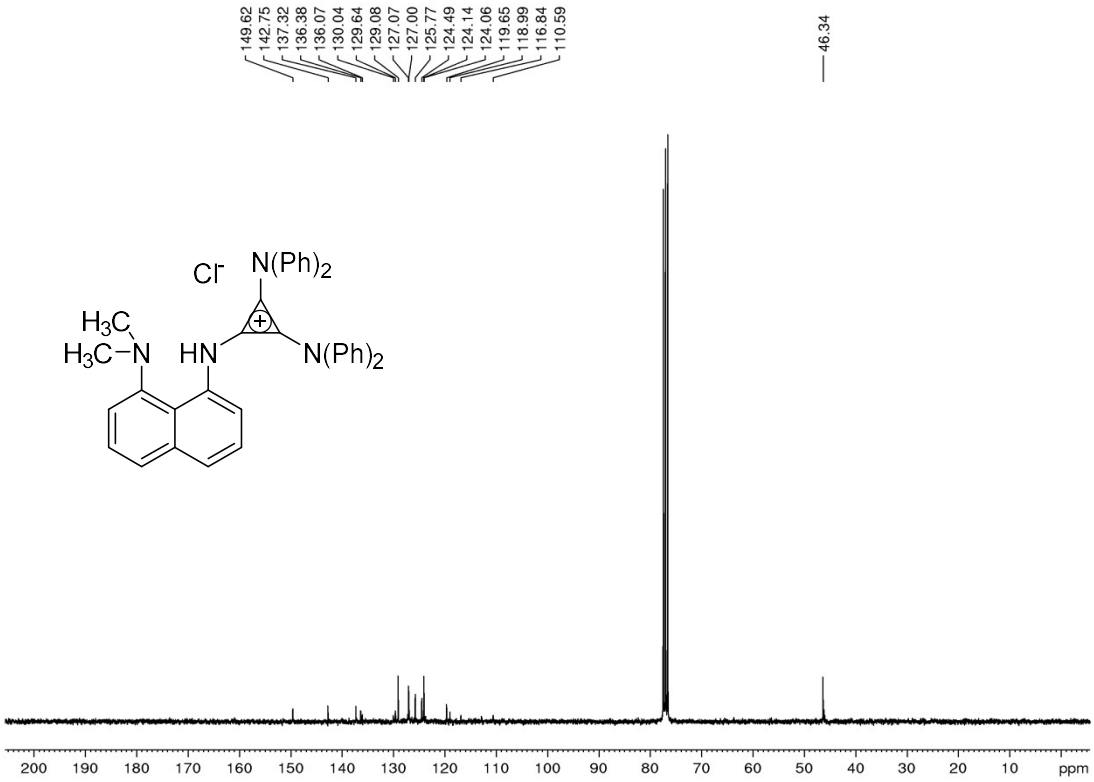

Figure S6. ^{13}C NMR spectrum of **7** in $CDCl_3$.

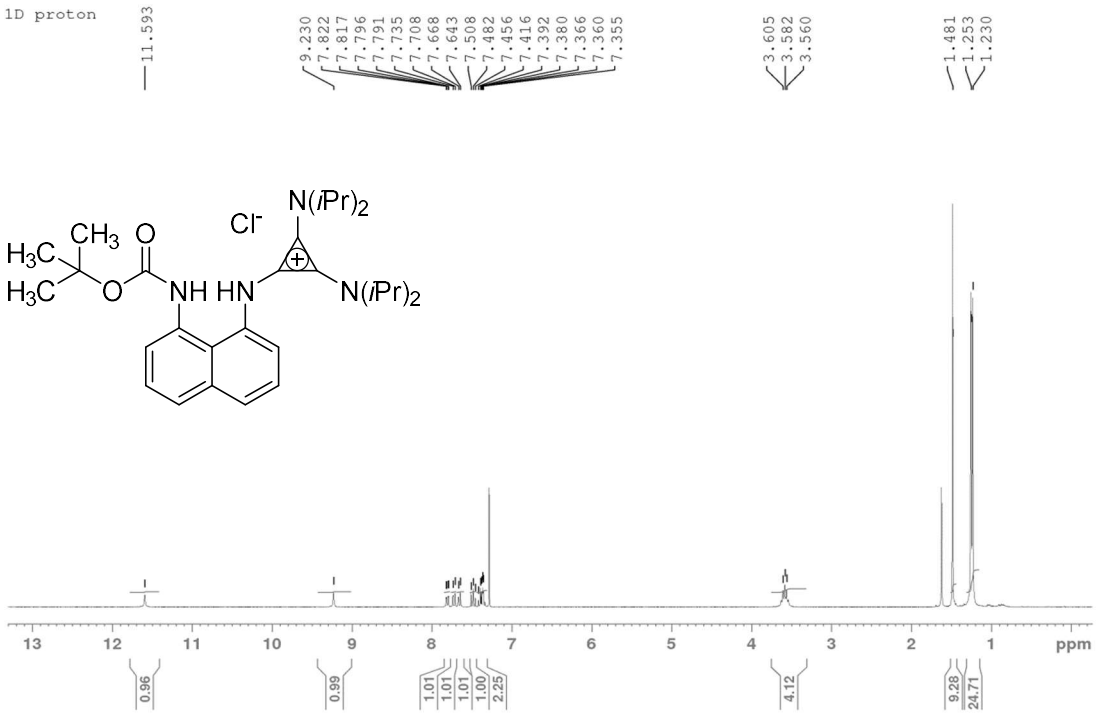

Figure S7. ^{1}H NMR spectrum of **8** in $CDCl_3$.

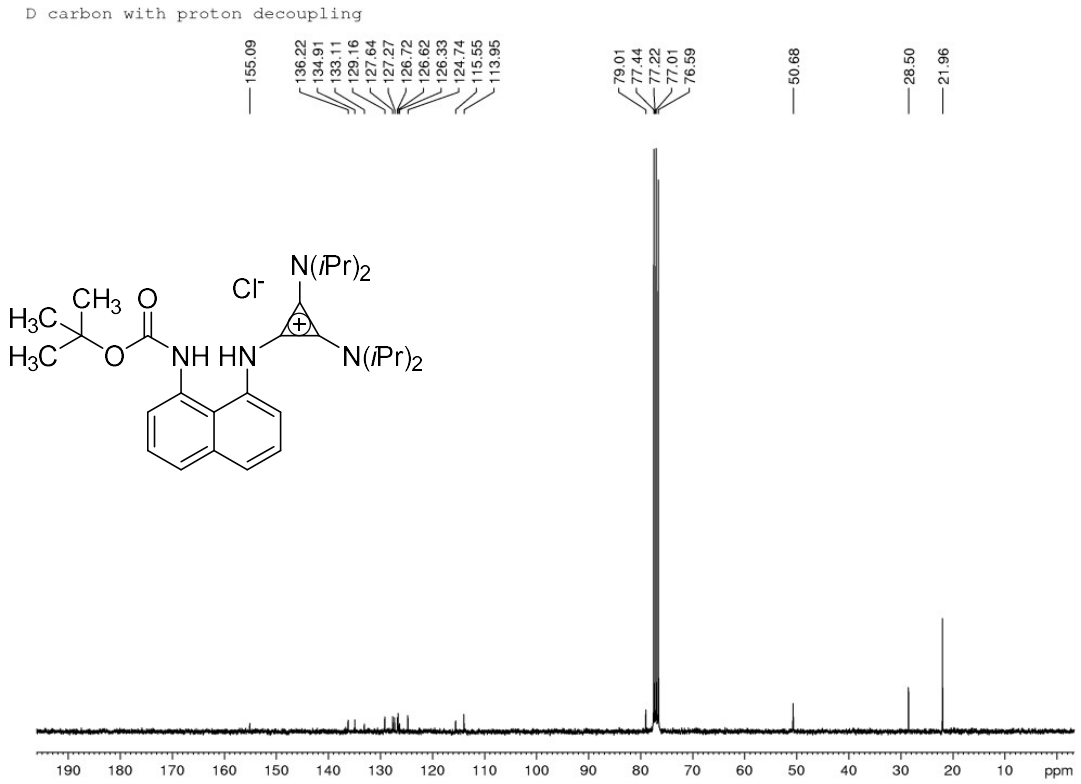

Figure S8. ^{13}C NMR spectrum of **8** in $CDCl_3$.

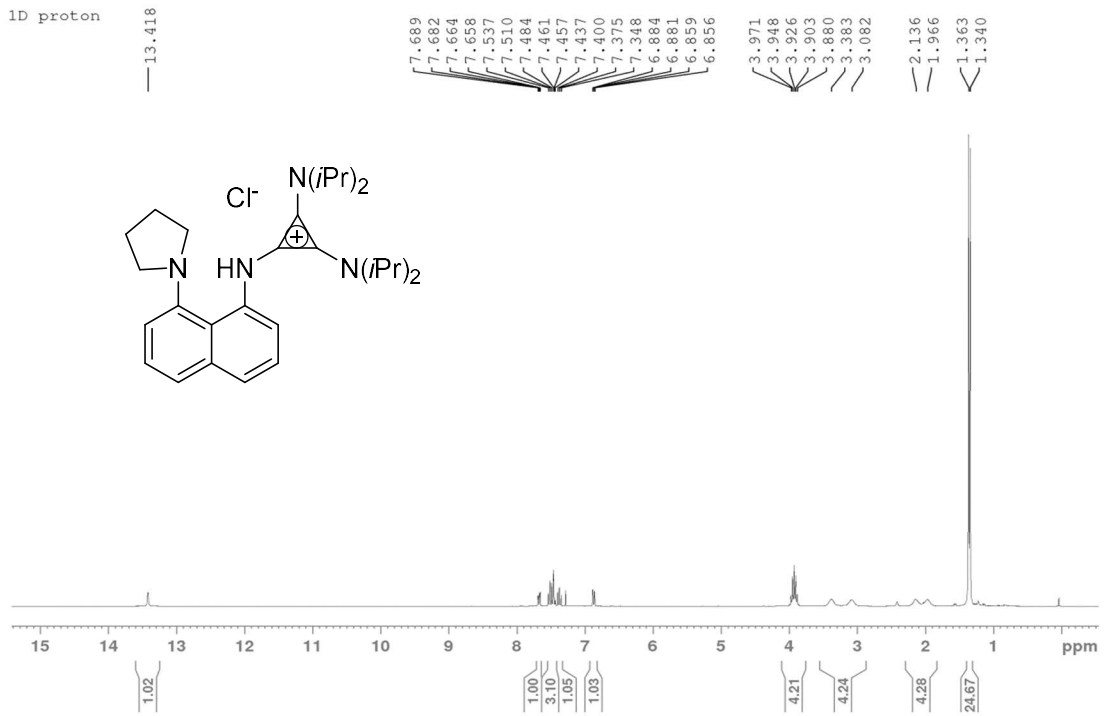

Figure S9. ^{1}H NMR spectrum of **9** in $CDCl_3$.

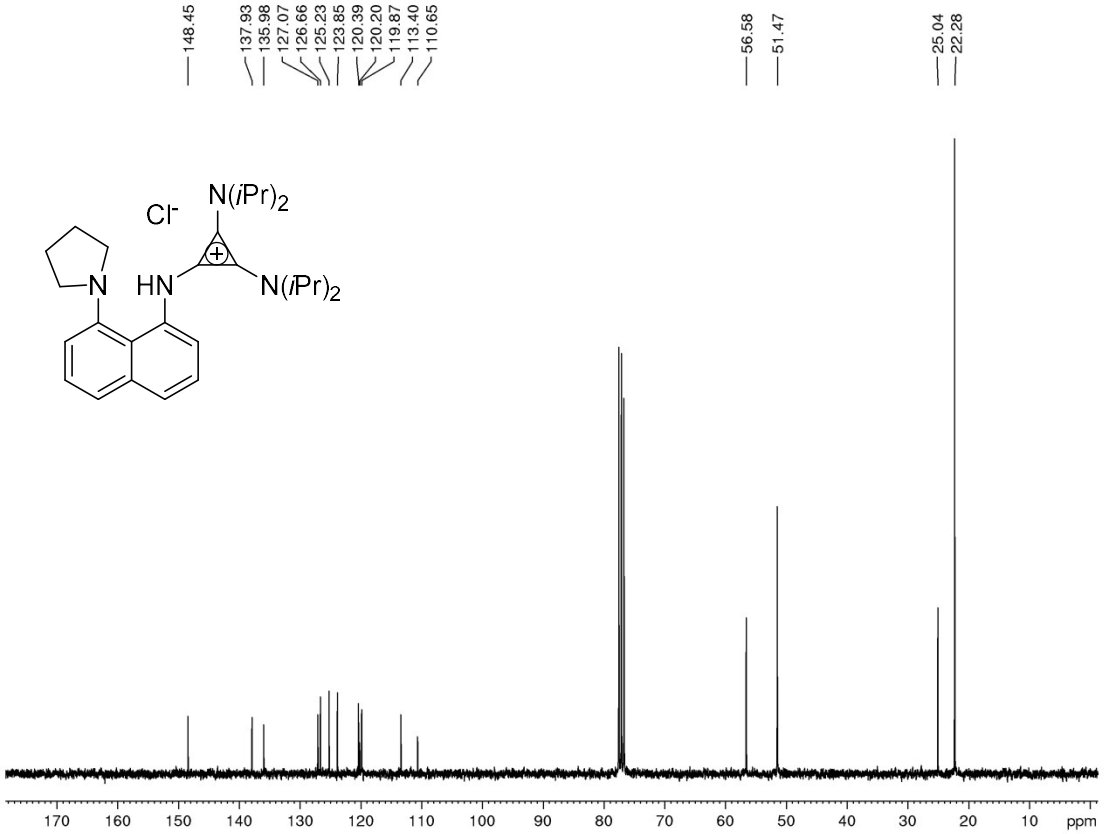

Figure S10. ^{13}C NMR spectrum of **9** in $CDCl_3$.

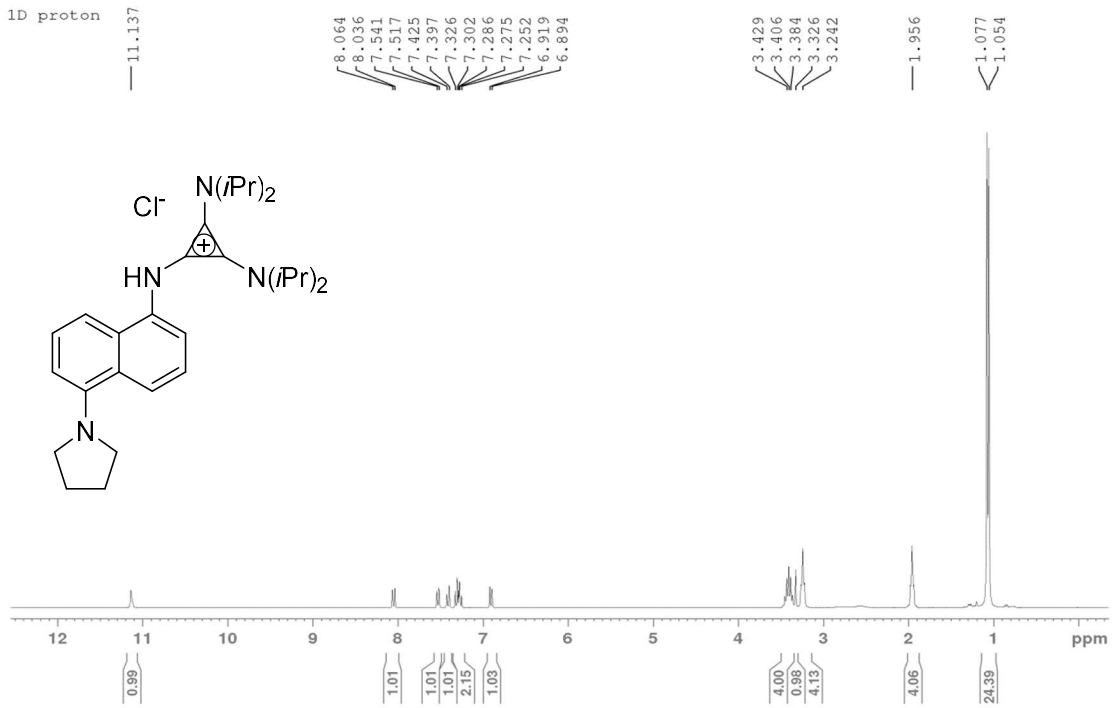

Figure S11. ^{1}H NMR spectrum of **10** in $CDCl_3$.

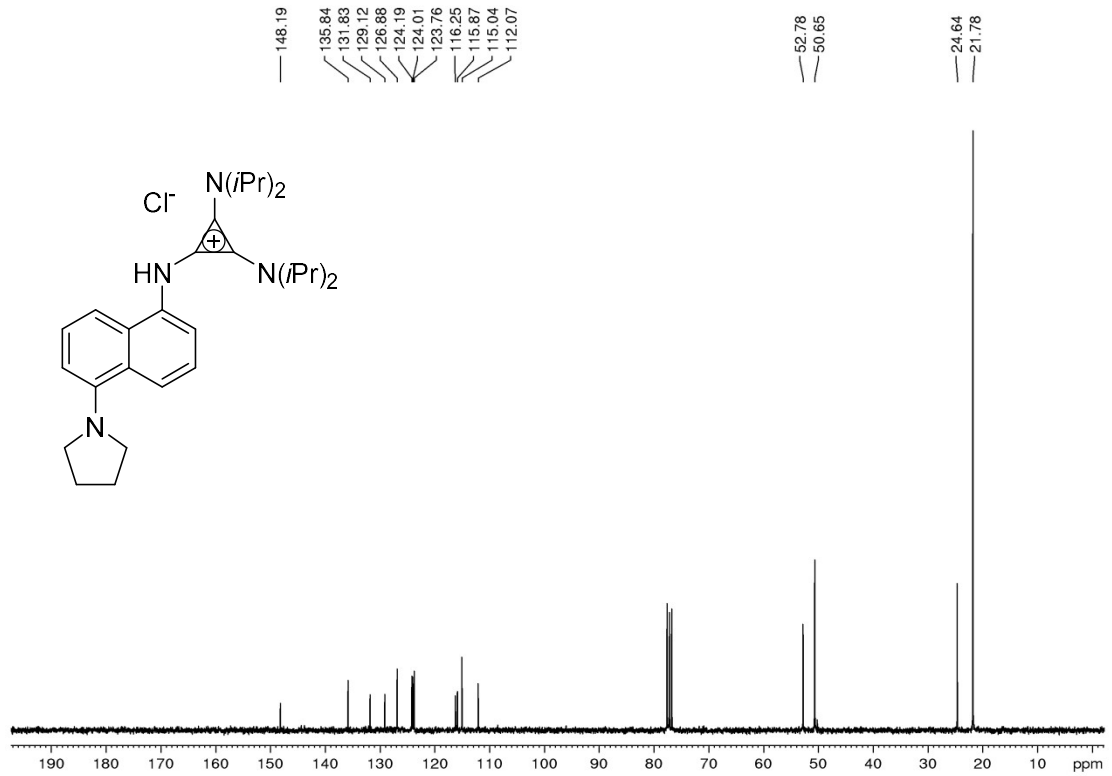

Figure S12. ^{13}C NMR spectrum of **10** in $CDCl_3$.

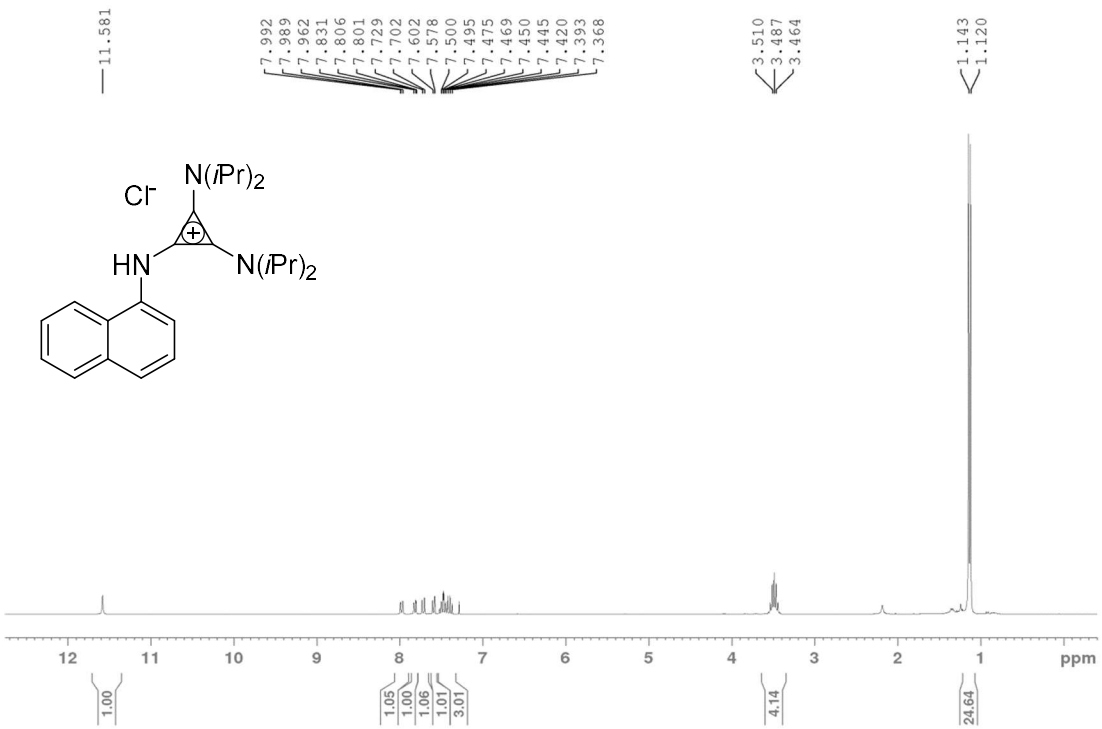

Figure S13. ^{1}H NMR spectrum of **11** in $CDCl_3$.

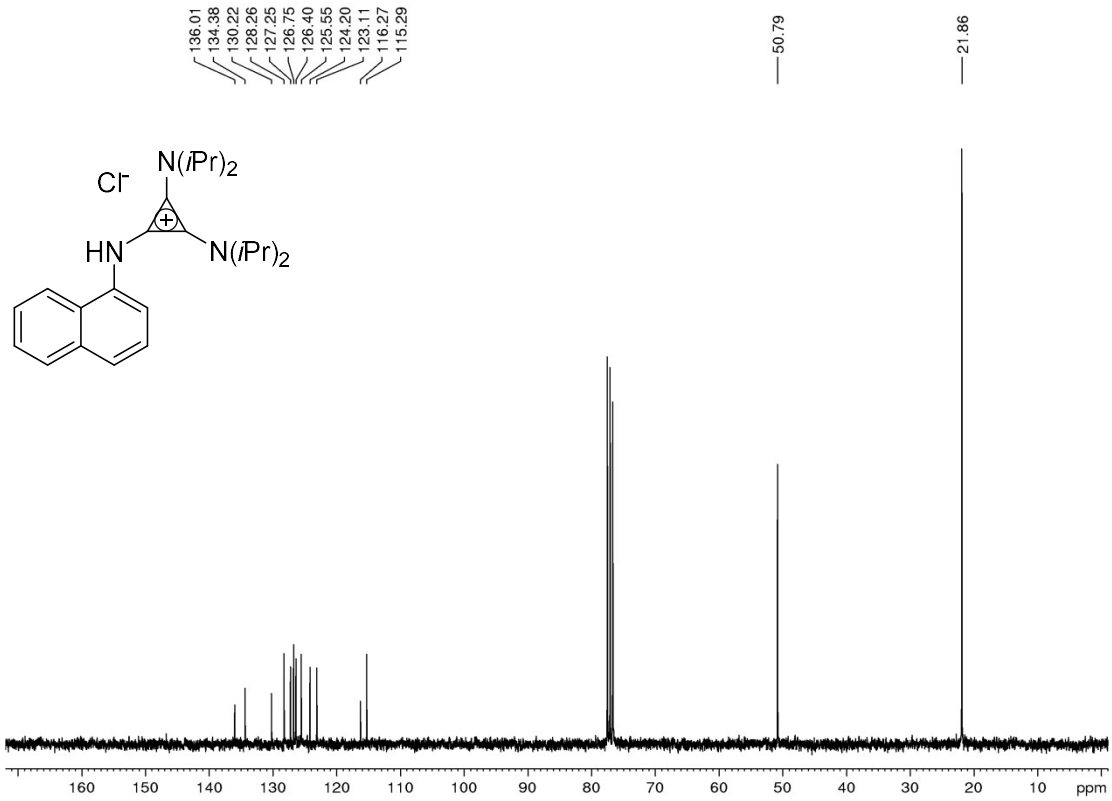

Figure S14. ^{13}C NMR spectrum of **11** in $CDCl_3$.

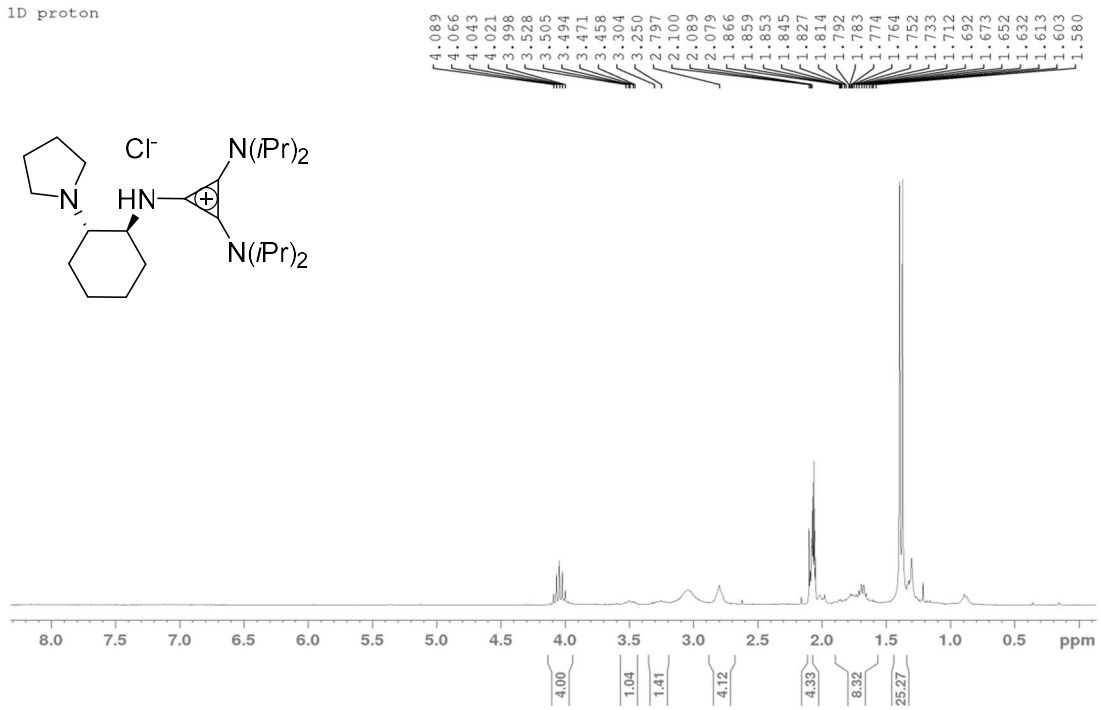

Figure S15. ^{1}H NMR spectrum of **12** in $CO(CD_3)_2$.

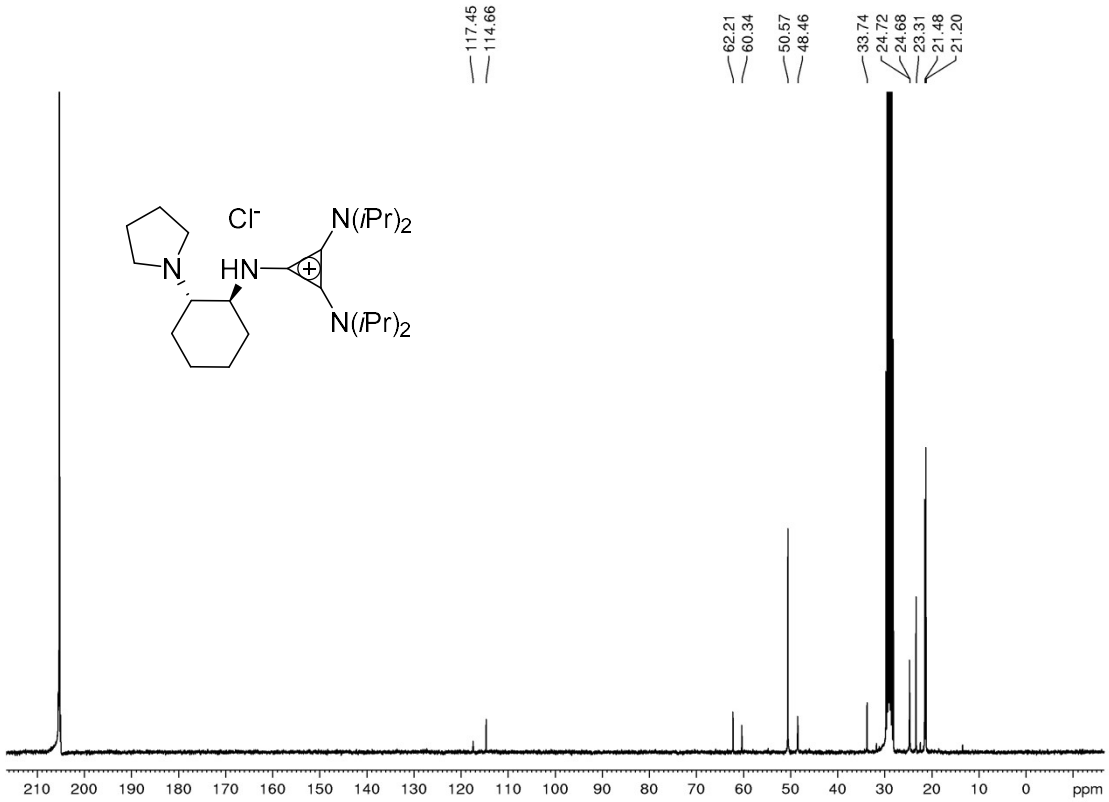

Figure S16. ^{13}C NMR spectrum of **12** in $CO(CD_3)_2$.

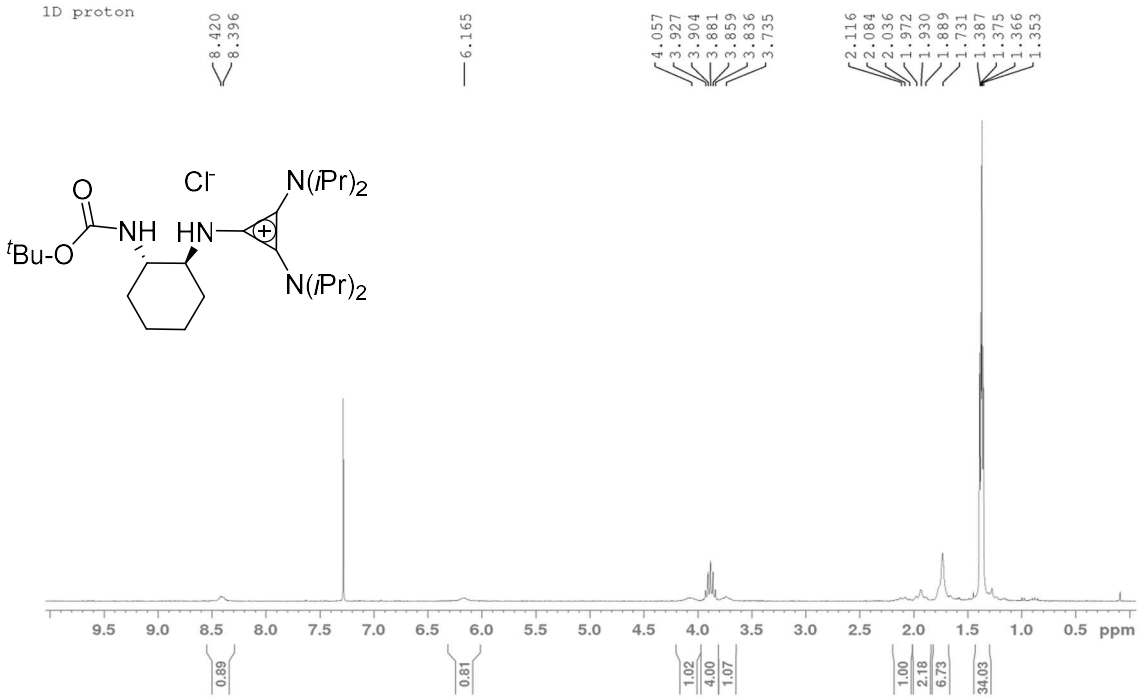

Figure S17. ^{1}H NMR spectrum of **13** in $CDCl_3$.

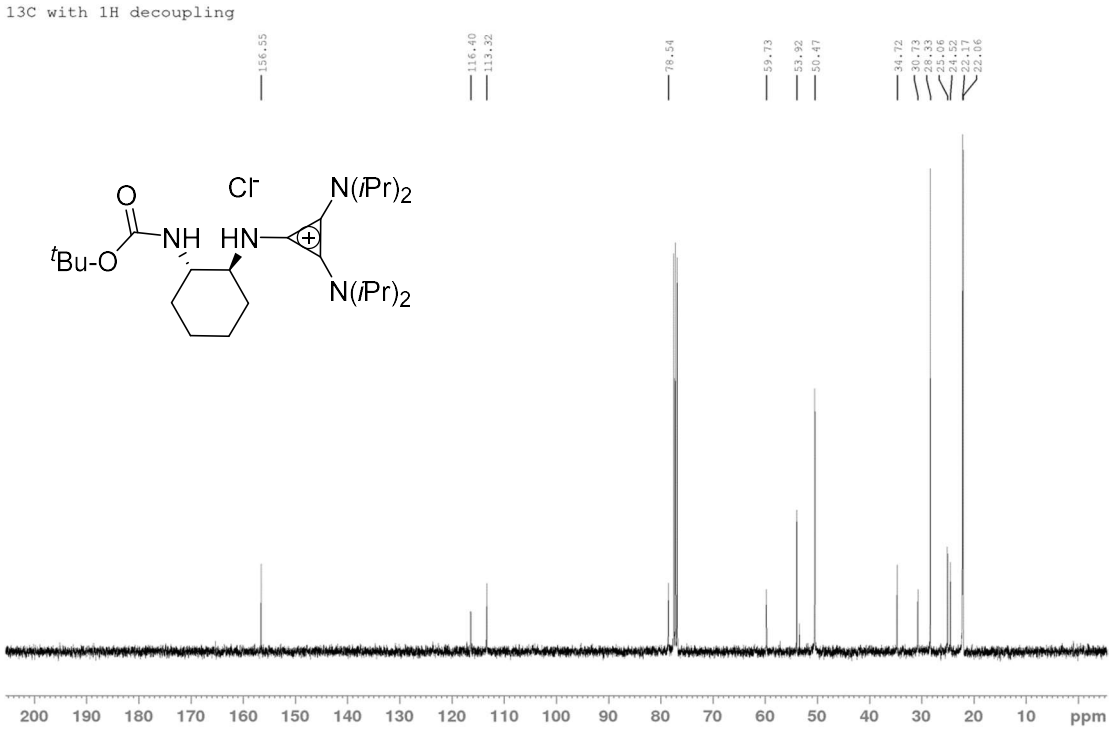

Figure S18. ^{13}C NMR spectrum of **13** in $CDCl_3$.

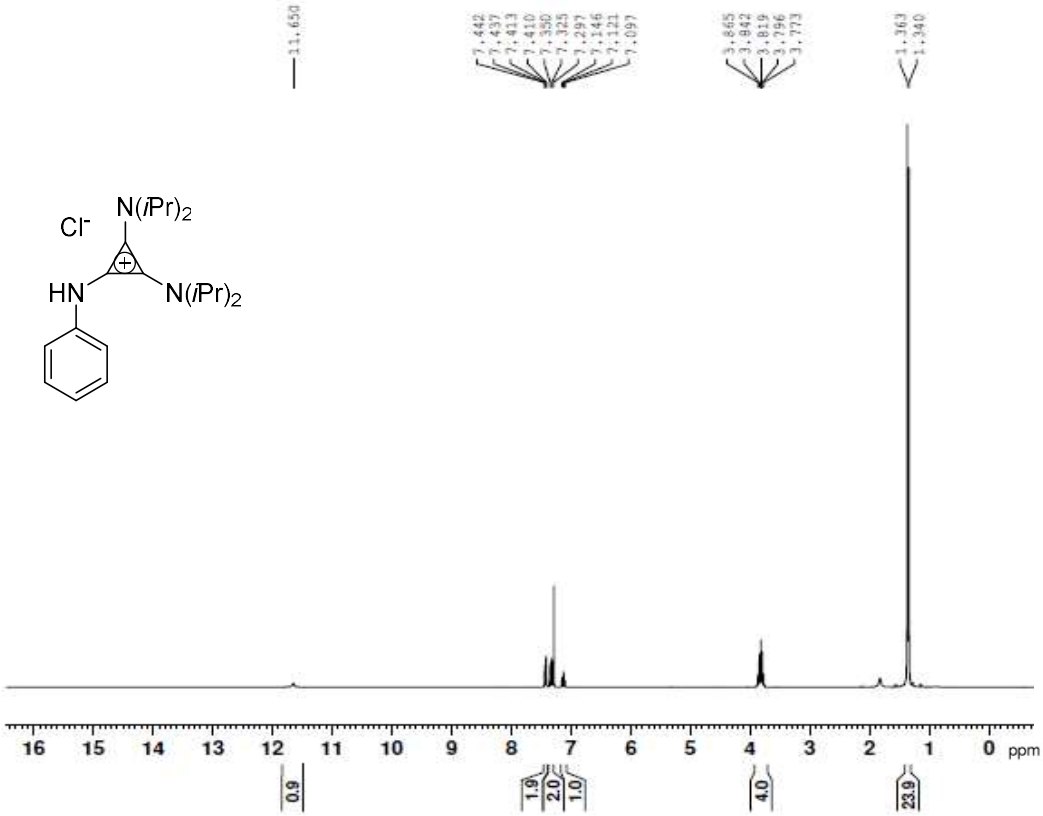

Figure S19. ^{1}H NMR spectrum of **14** in $CDCl_3$.

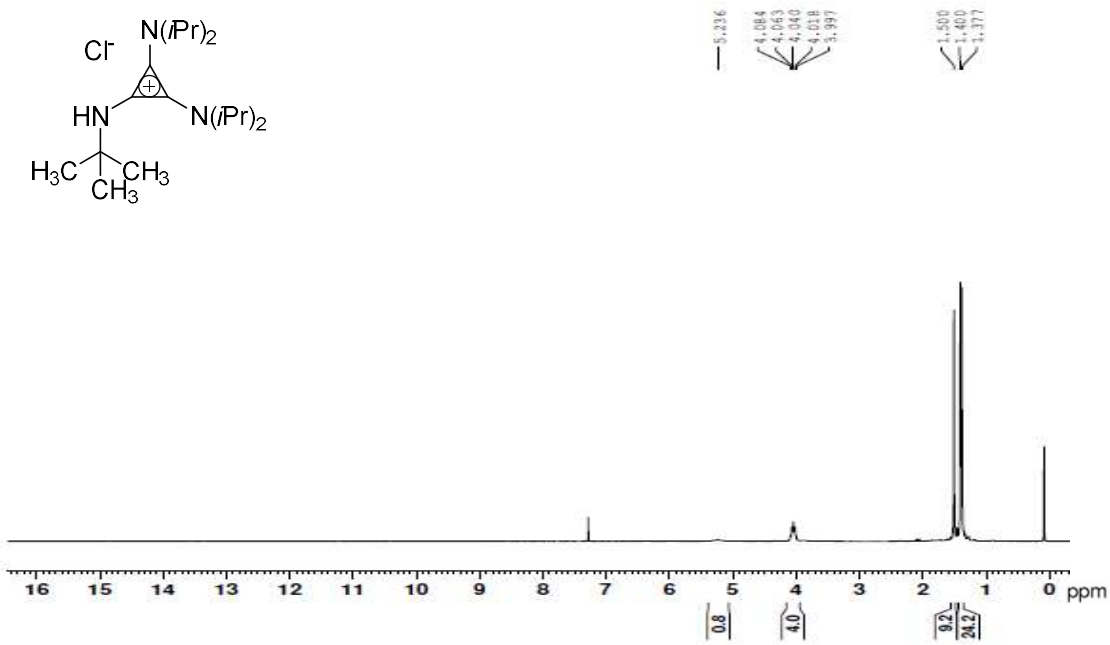

Figure S20. ^{1}H NMR spectrum of **15** in $CDCl_3$.

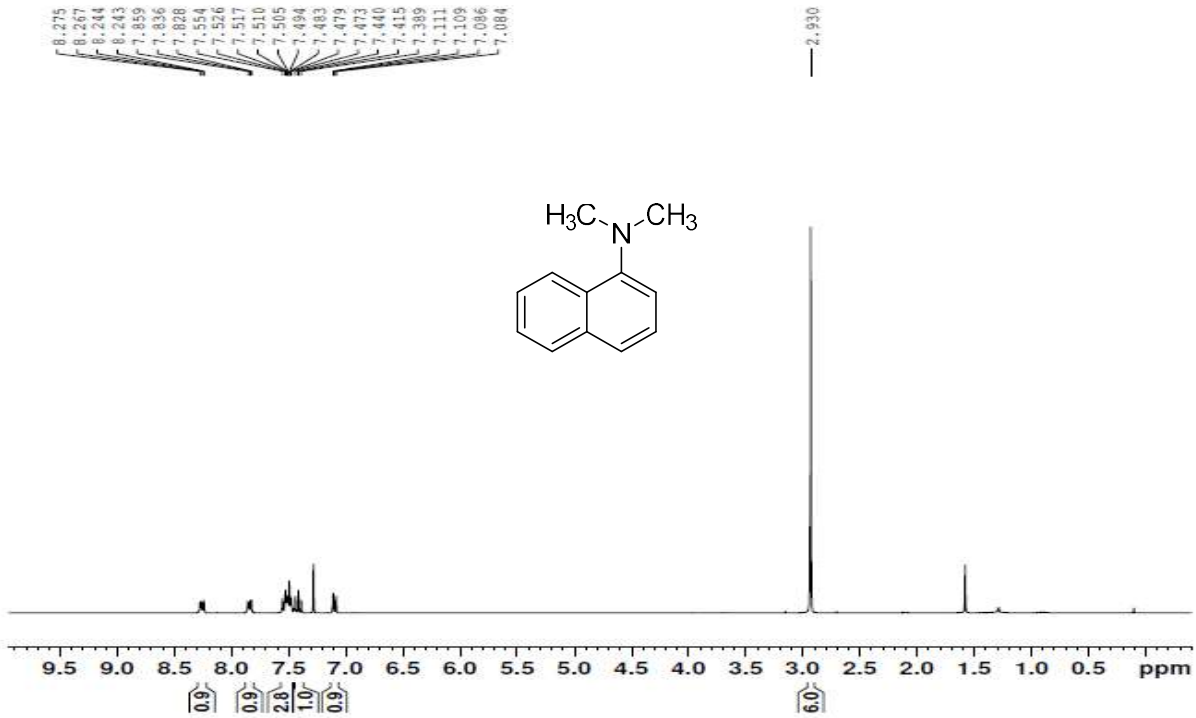

Figure S21. ^{1}H NMR spectrum of **16** in $CDCl_3$.

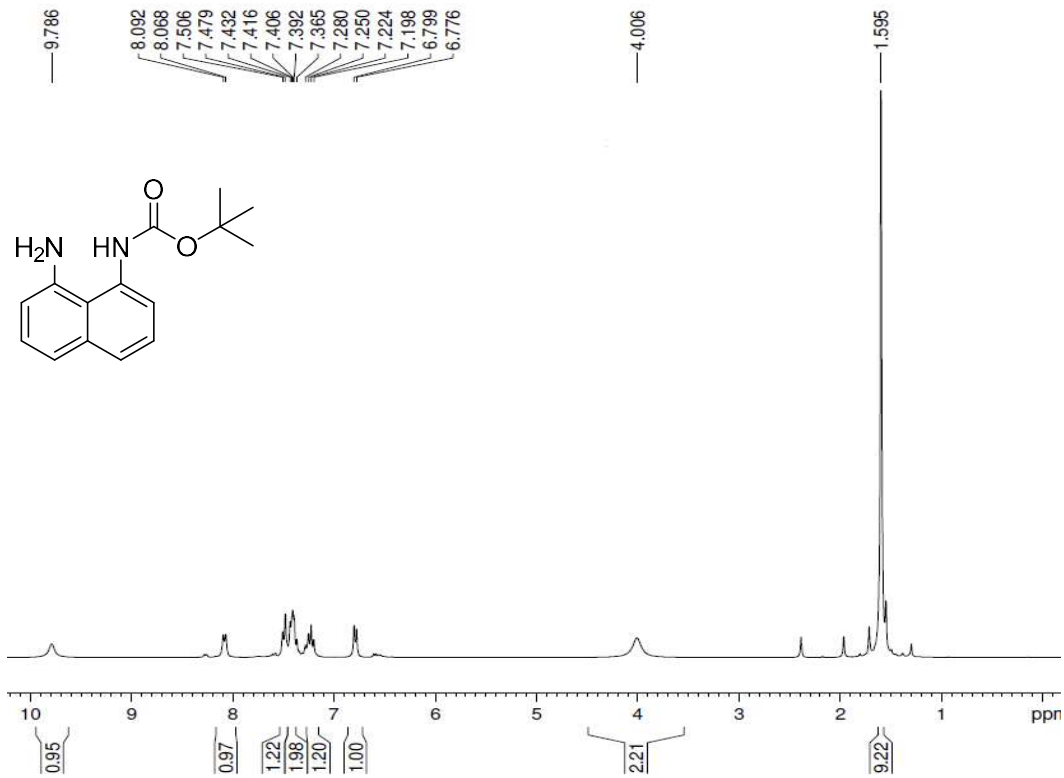

Figure S22. ^{1}H NMR spectrum of **17** in $CDCl_3$.

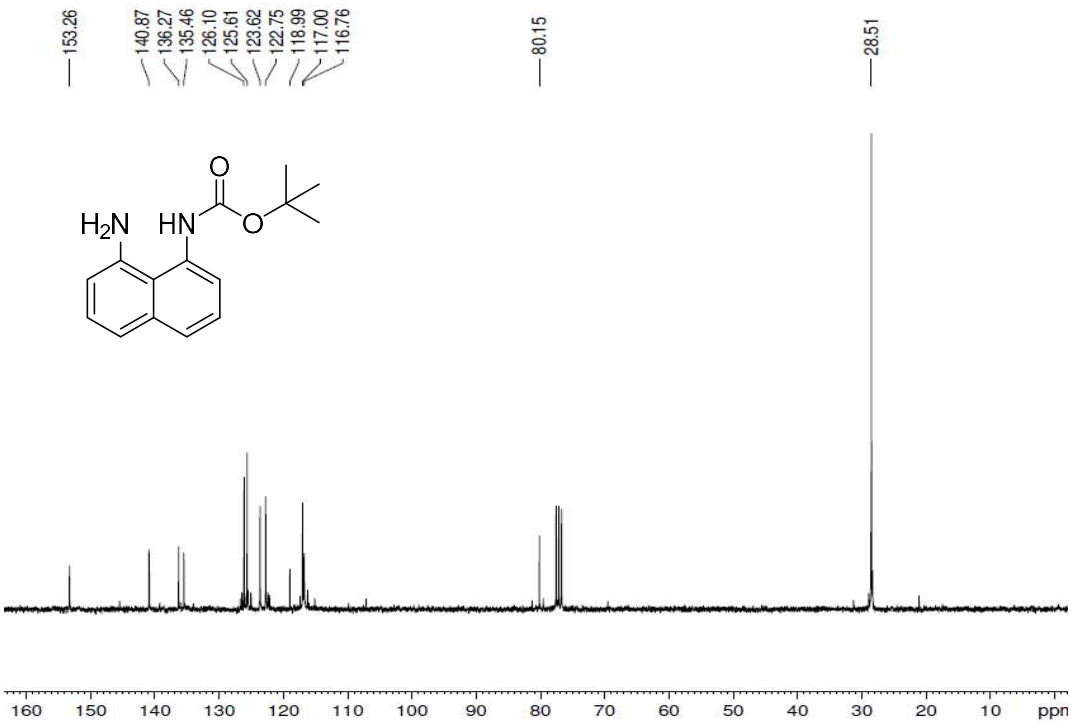

Figure S23. ^{13}C NMR spectrum of **17** in $CDCl_3$.

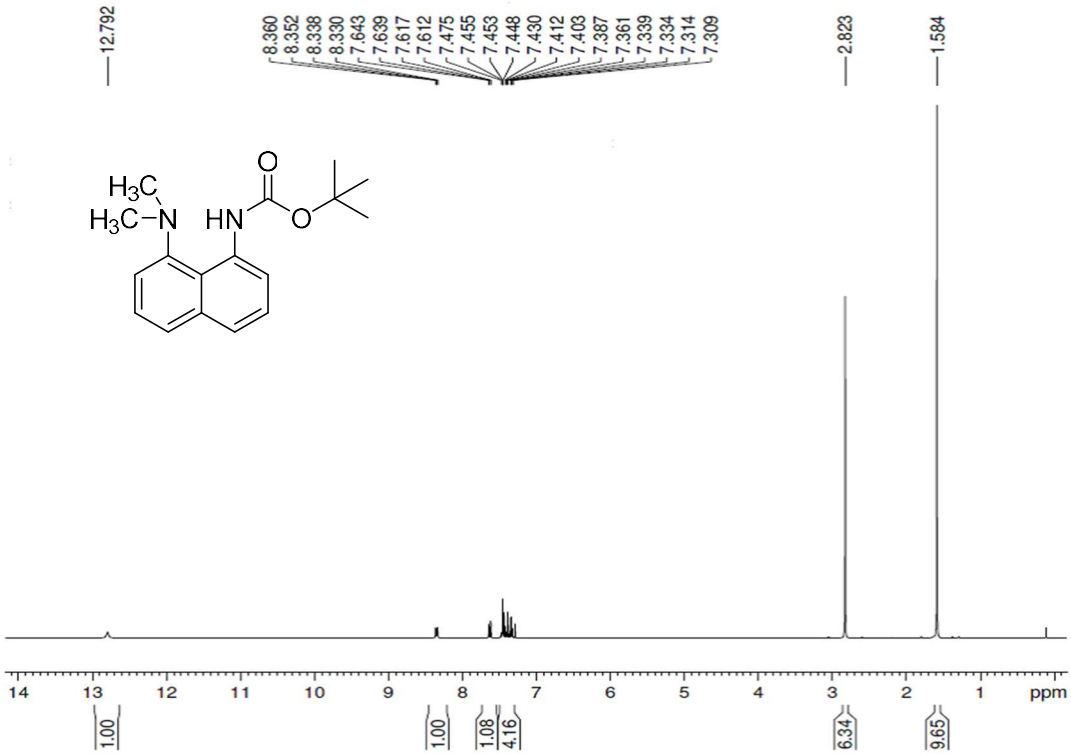

Figure S24. ^{1}H NMR spectrum of **18** in $CDCl_3$.

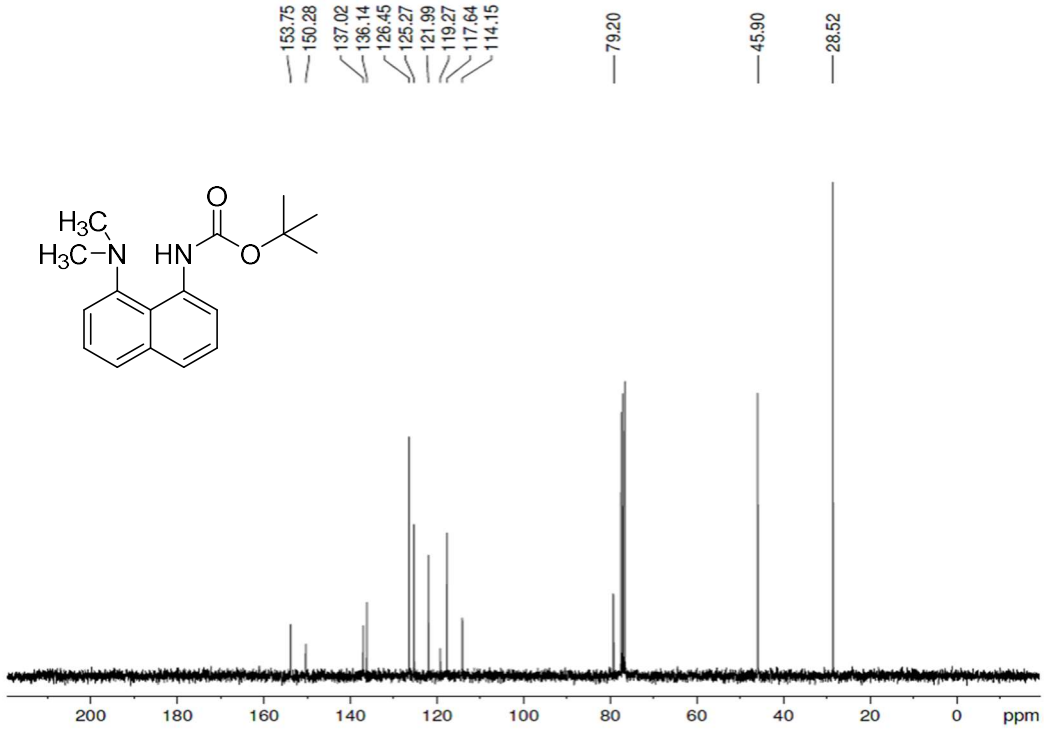

Figure S25. ^{13}C NMR spectrum of **18** in $CDCl_3$.

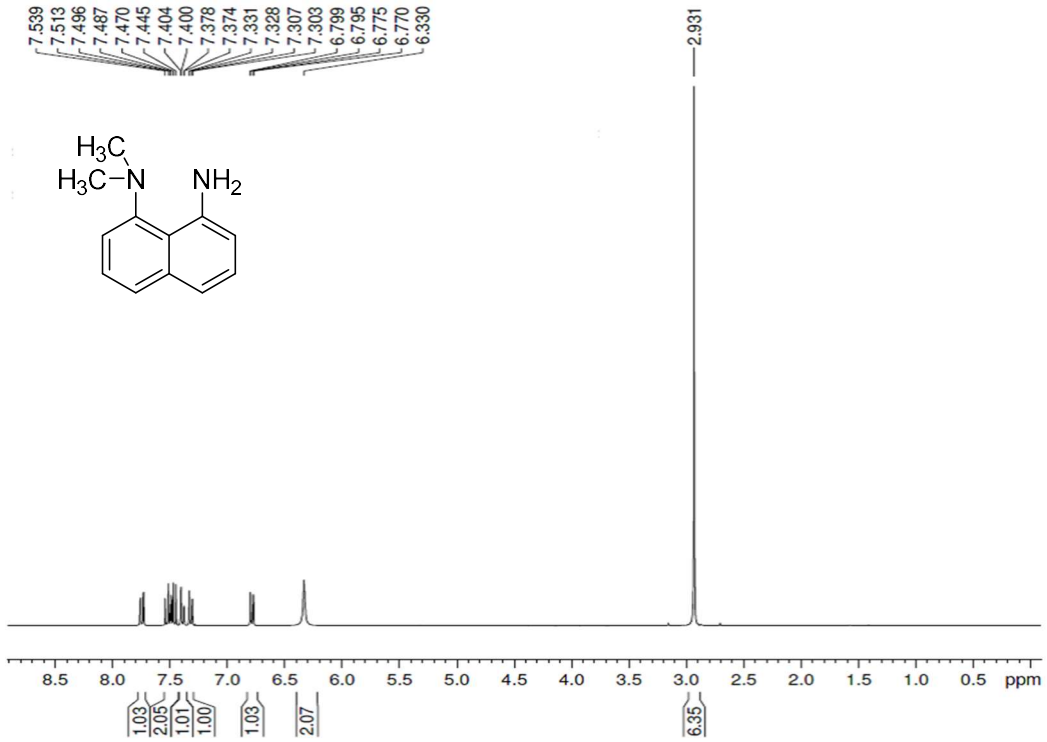

Figure S26. ^{1}H NMR spectrum of **19** in $CDCl_3$.

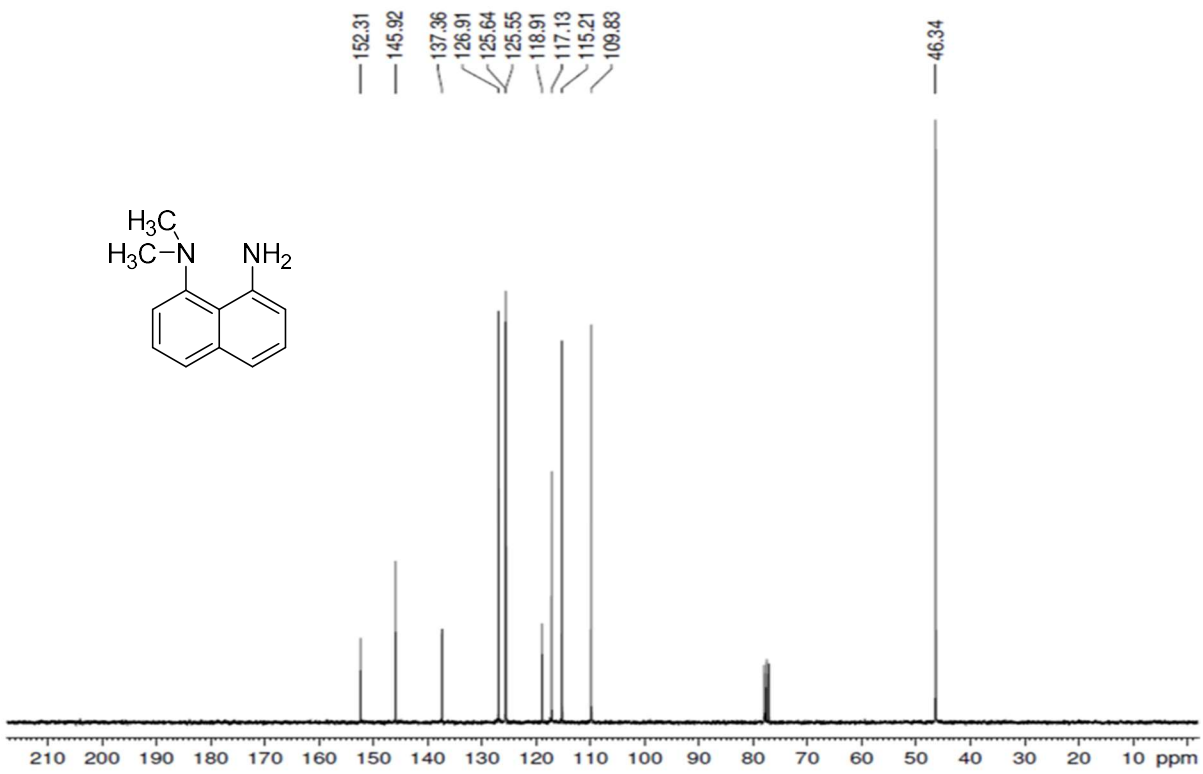

Figure S27. ^{13}C NMR spectrum of **19** in $CDCl_3$.

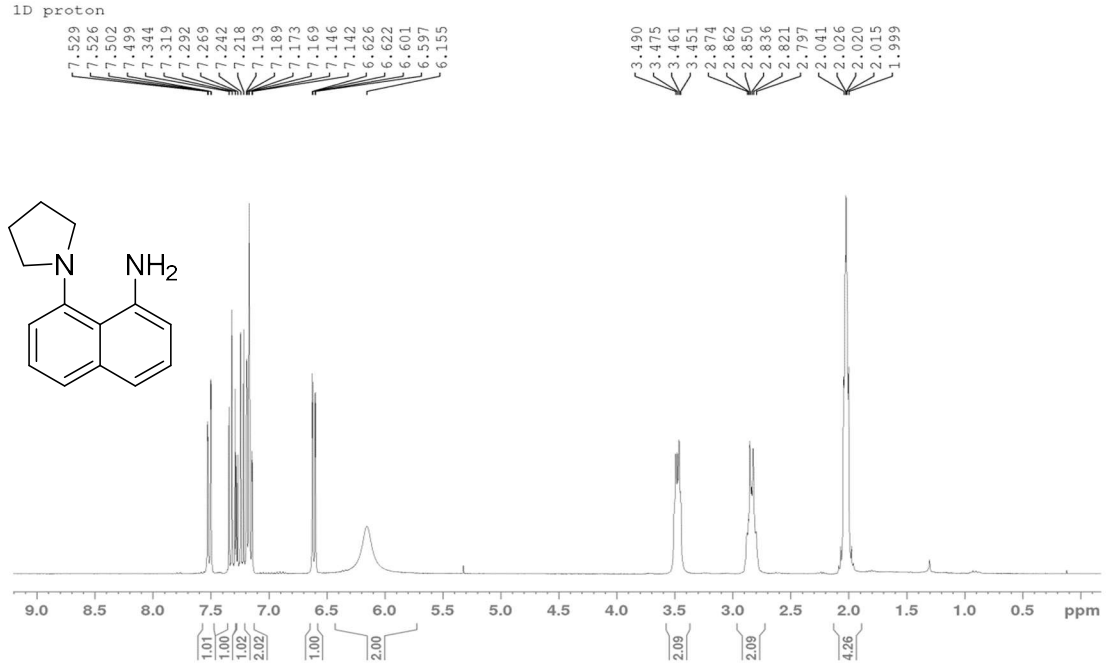

Figure S28. ^{1}H NMR spectrum of **20** in $CDCl_3$.

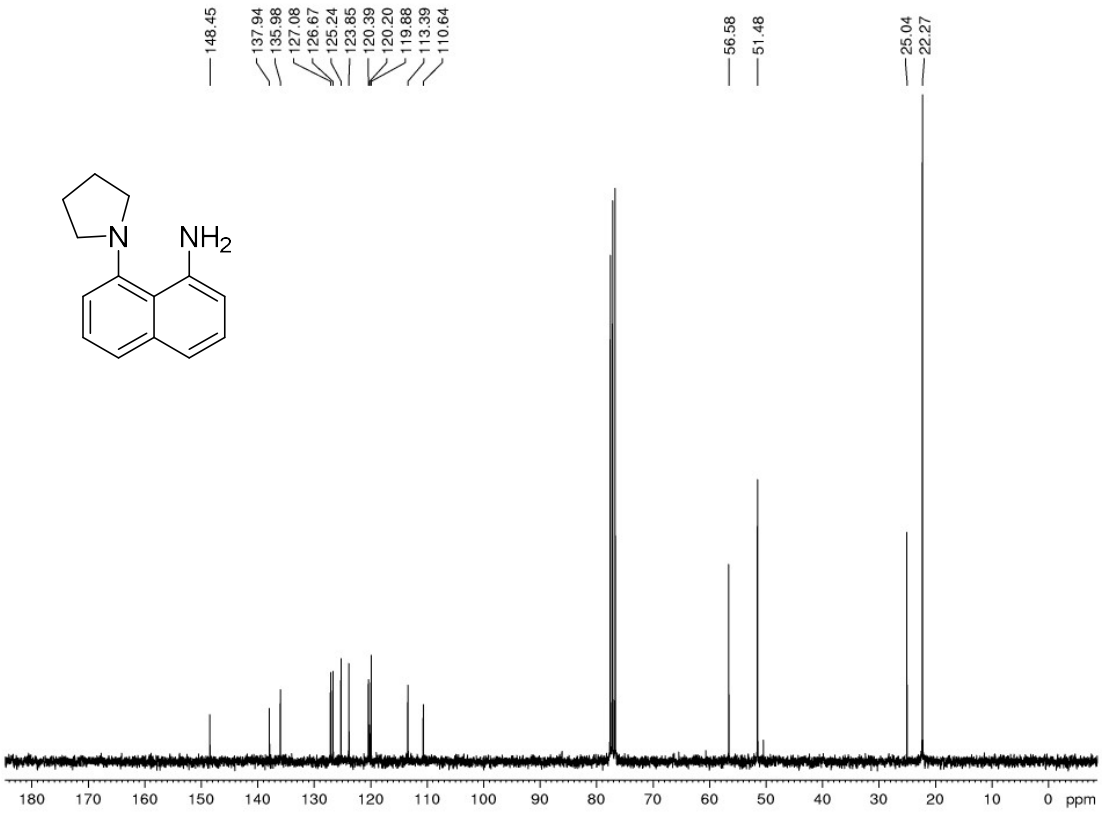

Figure S29. ^{13}C NMR spectrum of **20** in $CDCl_3$.

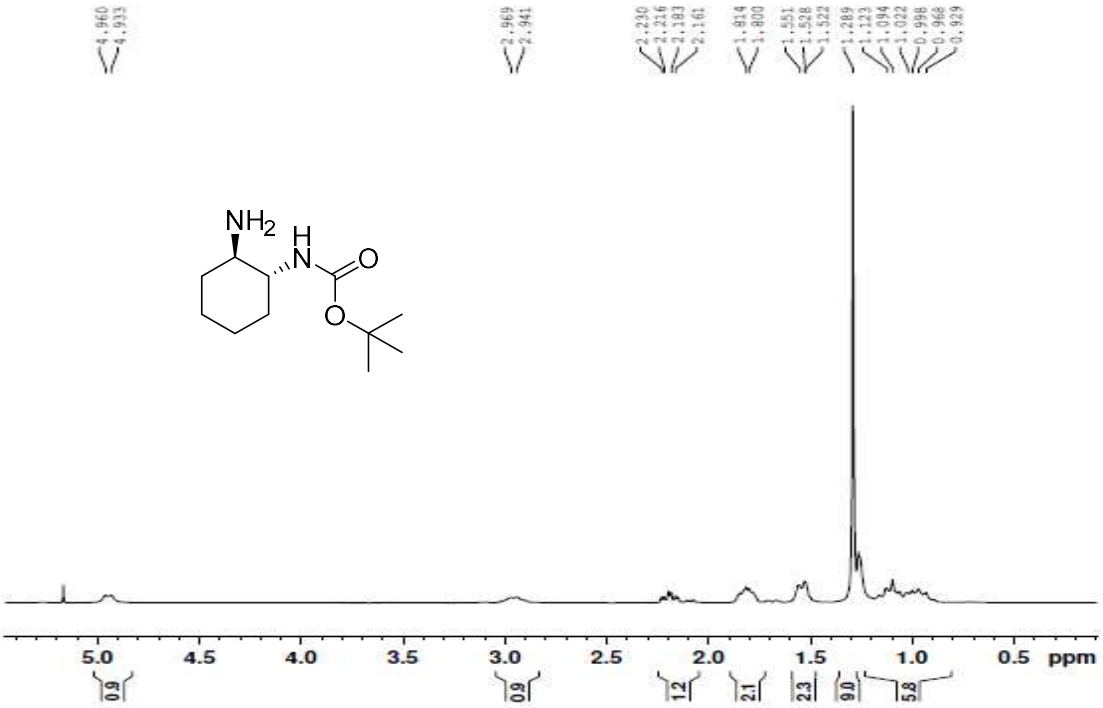

Figure S30. ^{1}HNMR spectrum of **21** in $CDCl_3$.

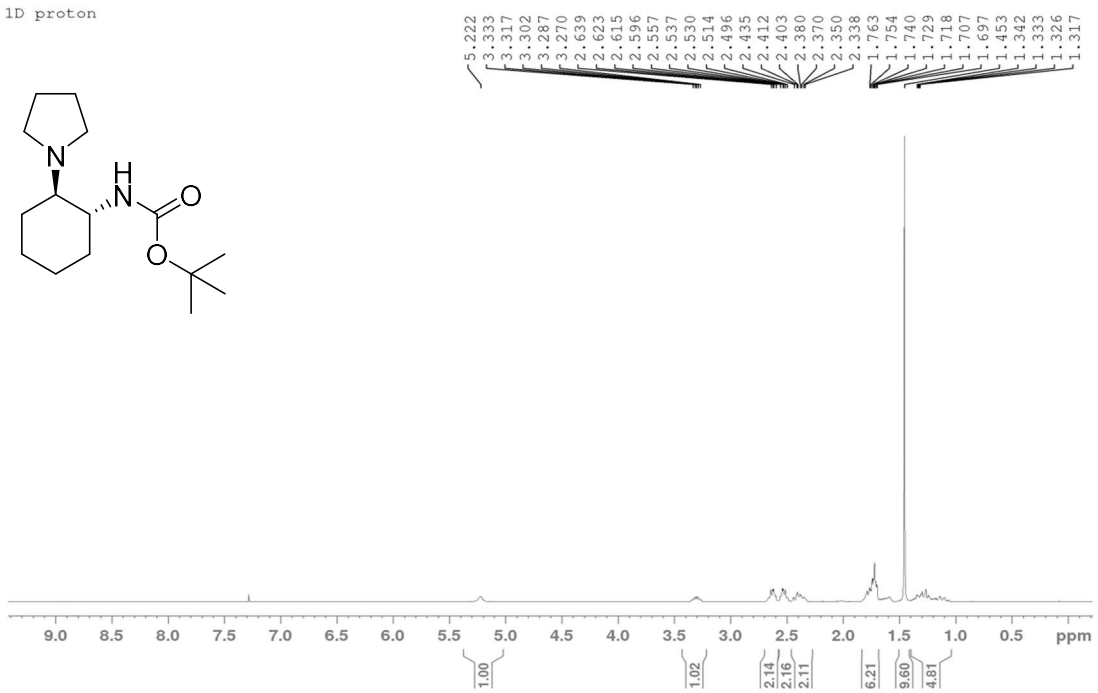

Figure S31. ^{1}H NMR spectrum of **22** in $CDCl_3$.

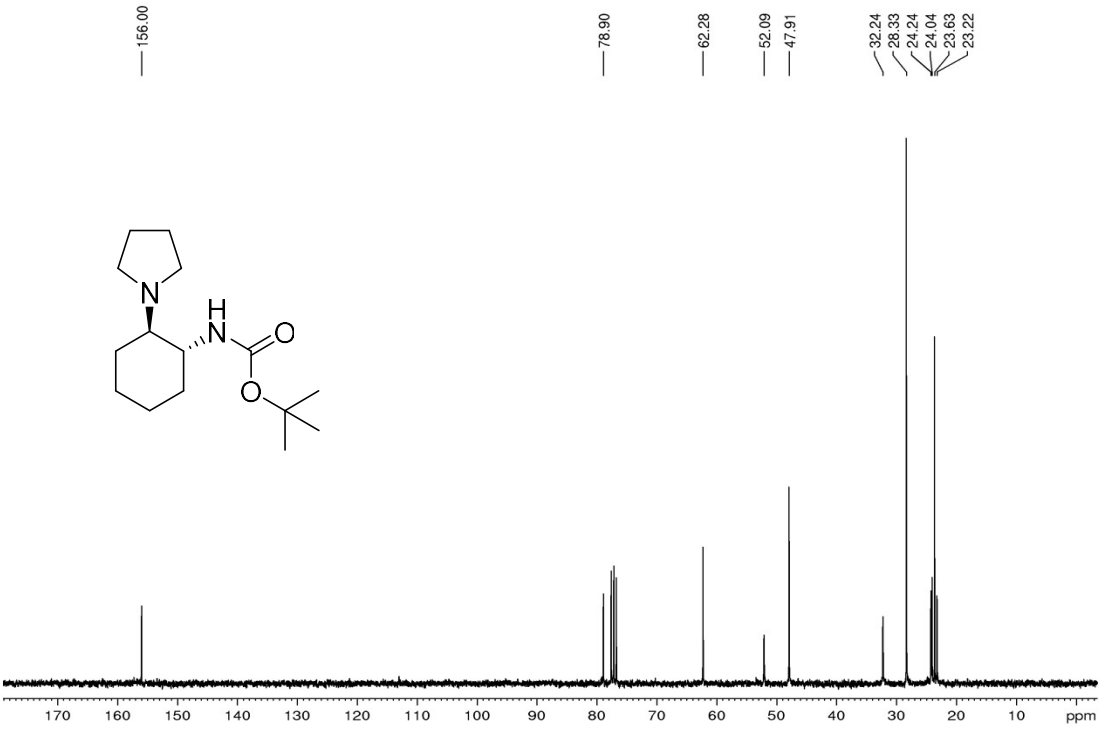

Figure S32. ^{13}C NMR spectrum of **22** in $CDCl_3$.

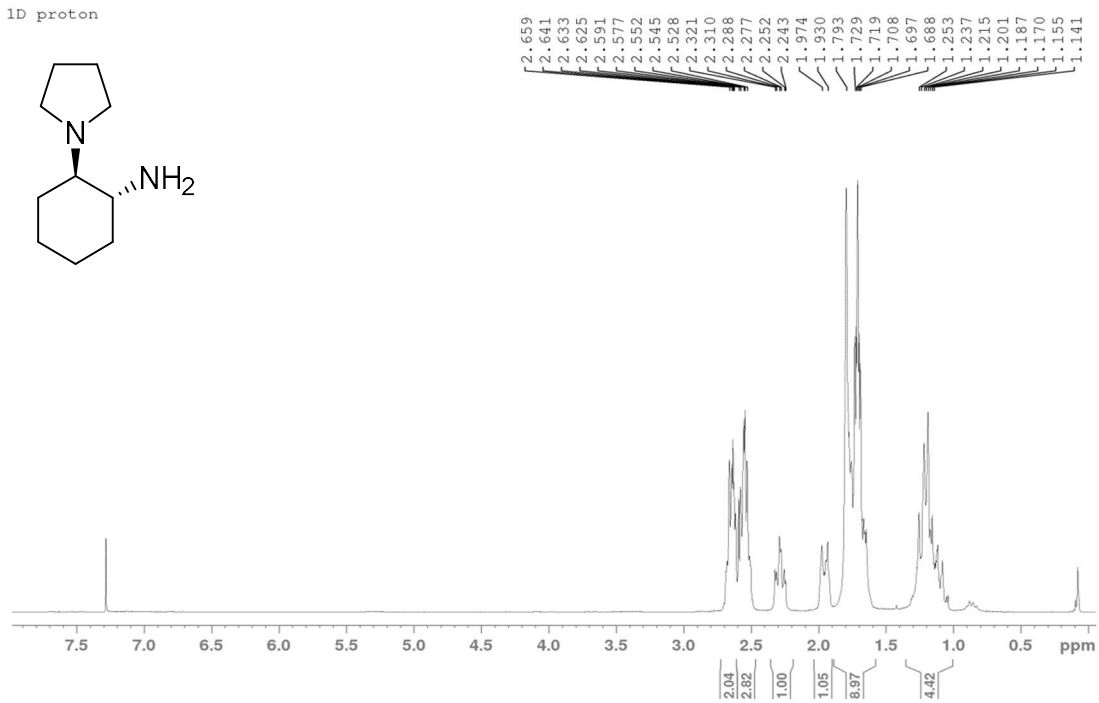

Figure S33. ^{1}H NMR spectrum of **23** in $CDCl_3$.

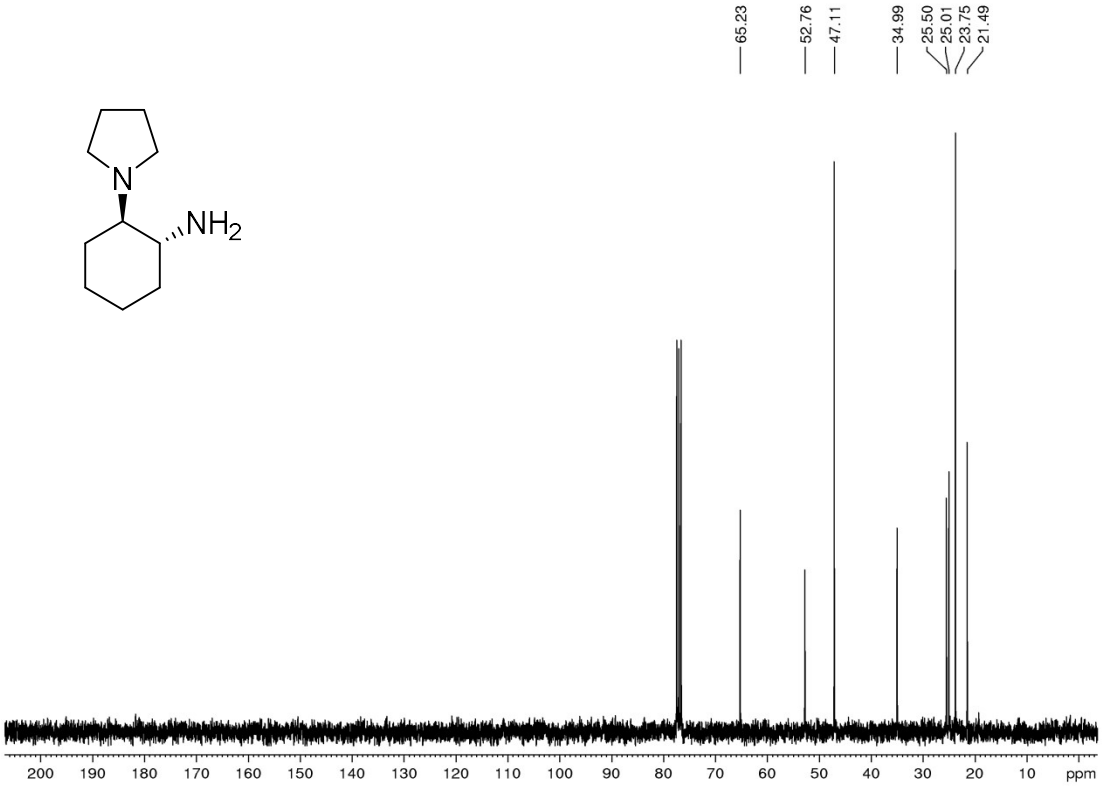

Figure S34. ^{13}C NMR spectrum of **23** in $CDCl_3$.

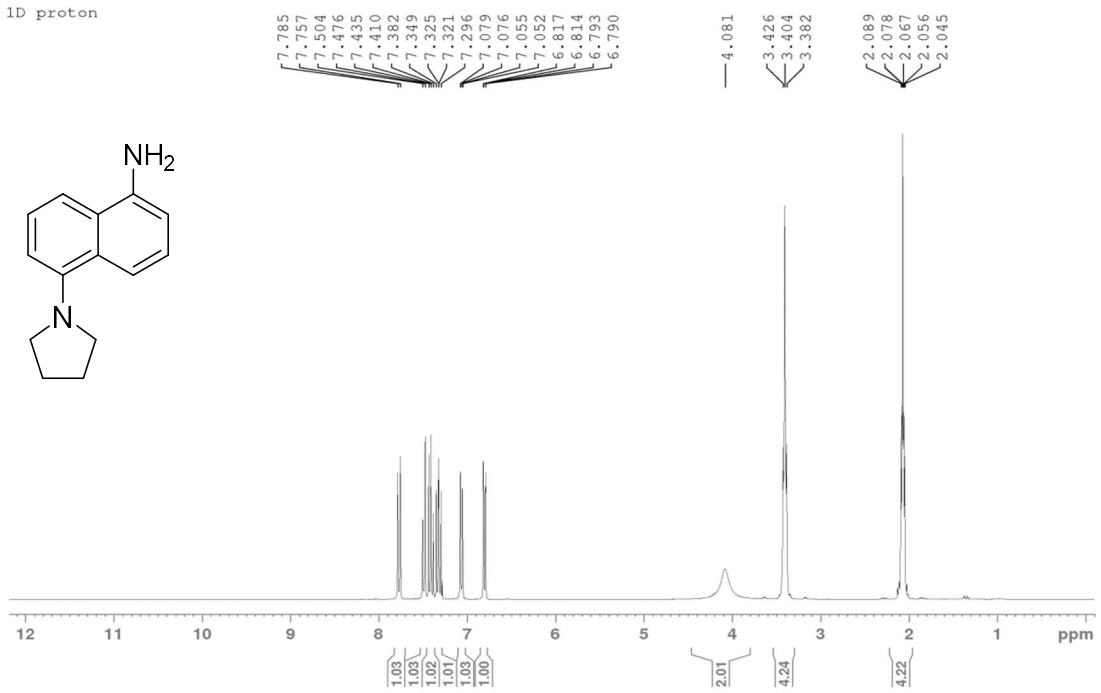

Figure S35. ^{1}H NMR spectrum of **24** in $CDCl_3$.

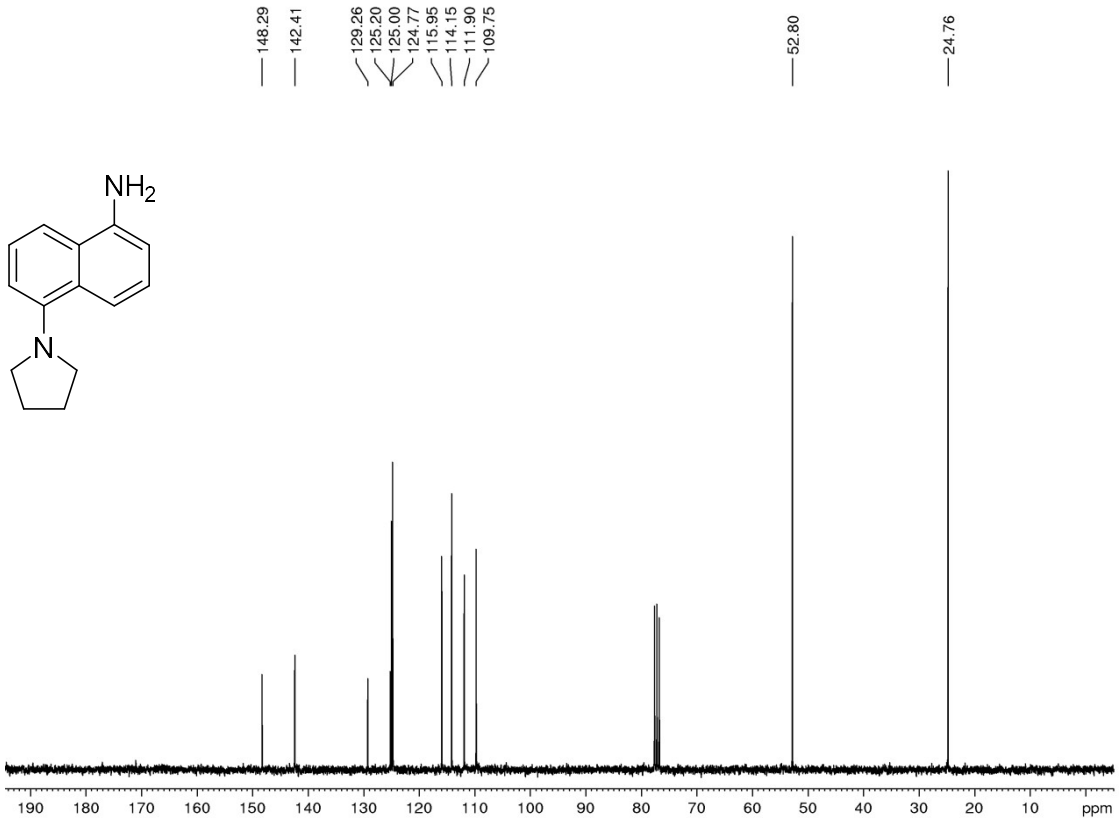

Figure S36. ^{13}C NMR spectrum of **24** in $CDCl_3$.

3.0 UV-vis absorption and fluorescence spectral data of 1, 6-16

Table S1. Fluorescence data of cyclopropenium-substituted amino compounds in ethanol.

Compound	λ_{max}	λ_{em}	Molar Attenuation Coefficient (ε) (M^{-1} cm^{-1})	Quantum Yield (ϕ)	Stokes Shift
1	334 nm	472 nm	4.70×10^3	0.37	138 nm
6	335 nm	476 nm	9.10×10^3	0.26	141 nm
7	345 nm	487 nm	1.66×10^4	0.18	142 nm
8	318/358 nm	414/448 nm	6.24×10^3	0.33	96 nm
9	333 nm	476 nm	8.60×10^3	0.43	143 nm
10	333 nm	435 nm	5.99×10^3	0.48	102 nm
11	320 nm	448 nm	8.80×10^2	0.11	128 nm
12	325 nm	468 nm	5.00×10^2	0.05	143 nm
13	323 nm	460 nm	1.80×10^2	0.08	137 nm
14	322 nm	468 nm	2.70×10^2	0.11	146 nm
15	322 nm	468 nm	2.00×10^2	0.09	146 nm
16	305 nm	416 nm	9.13×10^3	0.13	111 nm

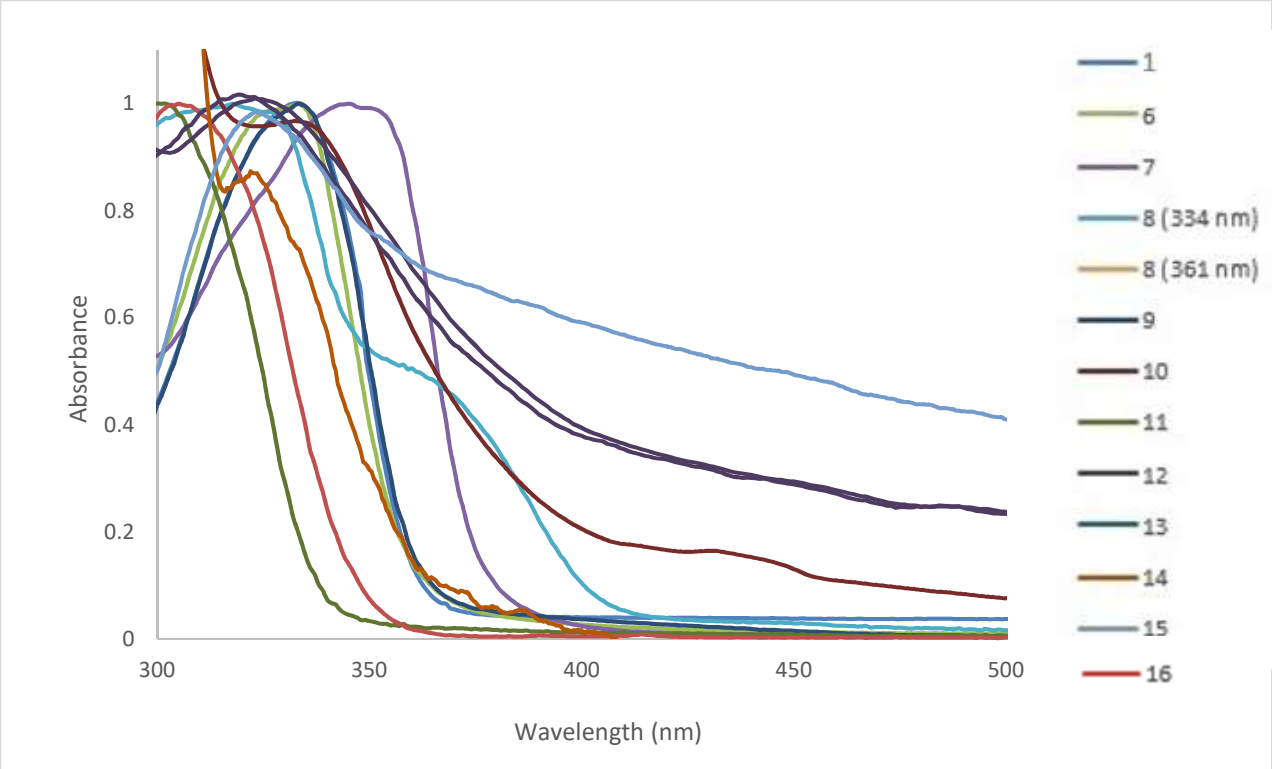

Figure S37. Normalized UV-vis absorption spectra of 1, 6-16 in EtOH.

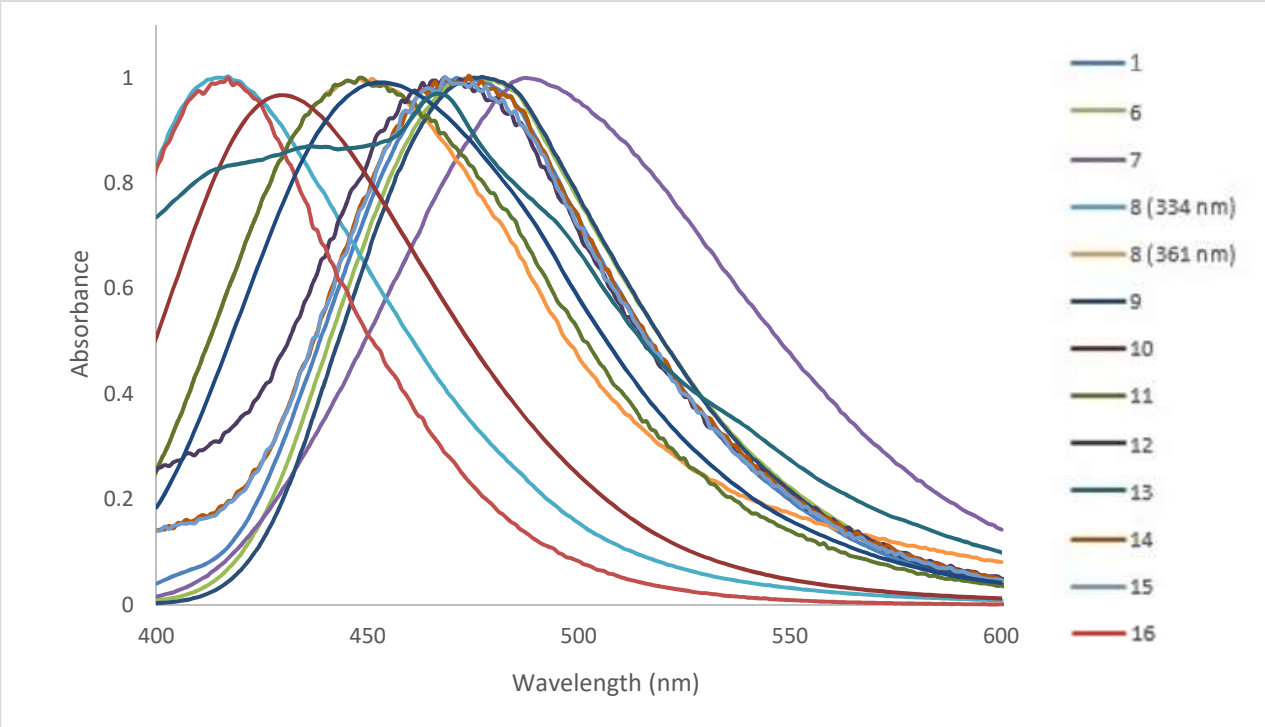

Figure S38. Normalized fluorescence emission spectra of 1, 6-16 in EtOH.

4.0 Computational methods and results

4.1 DFT Calculated Geometries and Thermochemical Data

4.1.1 Janus (**1**$_{in}$) Excited State

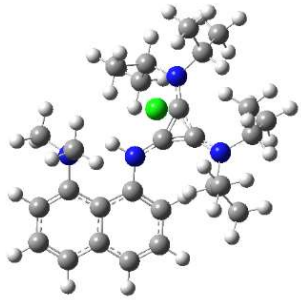

Figure S39. Computational model of Janus (**1**$_{in}$) excited state.

opt=calcfc freq=noraman td=singlets M062X/6-31+g(d,p) scrf=(smd,solvent=dichloromethane) geom=connectivity empiricaldispersion=gd3

Zero-point correction= 0.638315 (Hartree/Particle)
Thermal correction to Energy= 0.674425
Thermal correction to Enthalpy= 0.675369
Thermal correction to Gibbs Free Energy= 0.571323
Sum of electronic and zero-point Energies= -1731.501052
Sum of electronic and thermal Energies= -1731.464943
Sum of electronic and thermal Enthalpies= -1731.463999
Sum of electronic and thermal Free Energies= -1731.568044

N 0.90342300 -0.27637900 -0.41870300
H 1.32250100 -1.20468800 -0.05601600
N -1.91857800 2.04493700 0.04060500
N -2.43357400 -1.62956900 -0.59123200
C -0.41361900 -0.02580400 -0.39413000
C -1.49478300 0.82391300 -0.21625400
C -1.69101900 -0.55433100 -0.43171300
C 1.89492100 0.62358500 -0.69778400
C 3.25105500 0.26323500 -0.34212000
C 3.62838400 -0.96569500 0.22422200
C 4.98105800 -1.20081600 0.61213500
H 5.24944700 -2.15825600 1.04778800
C 5.93882800 -0.22395500 0.42461500
H 6.96653700 -0.40697900 0.72496800
C 5.59278500 1.00733200 -0.15988100
H 6.34371500 1.77877100 -0.30373000
C 4.26081400 1.27212400 -0.56094000
C 3.90148900 2.49708800 -1.16657300
H 4.67854700 3.24096000 -1.32120400
C 2.58292500 2.75848500 -1.62451300
H 2.36826900 3.67529700 -2.16438700
C 1.59302200 1.83809500 -1.39958500
H 0.58468800 1.98582300 -1.77493400
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H 3.48971900 -3.10264700 2.02755200
H 3.76553300 -3.62341500 -0.46841700
H 2.78297300 -2.66751600 -1.60969800
N 2.64453200 -2.01704500 0.38666700

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H 1.99167800 -3.80761800 -0.49178600
C -0.93078200 3.06190500 0.47915100
C -1.21017100 3.50814900 1.91203500
C -0.88141400 4.23243700 -0.49799500
H -1.23093400 2.64431800 2.58262600
H -0.70436500 3.88942900 -1.52182900
C -3.35740000 2.38911700 0.04455200
C -3.97867600 2.10493600 -1.32052600
C -4.08154900 1.73589300 1.22075700
H -3.90847000 1.04783400 -1.59419900
C -1.75394000 -2.92704400 -0.82666200
C -0.92844100 -2.88561300 -2.10962500
C -0.92788300 -3.33317200 0.38910900
H -1.54446500 -2.58247200 -2.96149800
H -1.54829200 -3.38195600 1.28807500
C -3.90641700 -1.59269200 -0.48782600
C -4.38304000 -2.39097200 0.72177300
C -4.55411100 -2.04804400 -1.79236600
H -4.18848300 -1.45675300 -2.63734800
Cl -0.91419300 -0.32461200 2.95508000
H -0.06528800 4.90353200 -0.21347900
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H -2.15828100 4.05086300 1.98831100
H -0.41076300 4.18284300 2.23276500
H -3.47303100 2.68983900 -2.09488200
H -5.03656900 2.38198000 -1.31060300
H -3.68723500 2.10946800 2.16939600
H -5.15043900 1.96483600 1.17177900
H -3.95920100 0.64983000 1.22267900
H -5.46775800 -2.28625200 0.81992100
H 0.03446000 2.54952500 0.47282400
H -3.38267600 3.47137800 0.19490700
H -4.15940400 -0.54489400 -0.33111300
H -2.56070800 -3.65134900 -0.95882400
H -3.91174600 -2.02355500 1.63806800
H -4.15623700 -3.45664600 0.61257200
H -5.63753600 -1.91488500 -1.72024700
H -4.36183100 -3.10648200 -1.99426800
H -0.51970200 -3.87995800 -2.31244900
H -0.08670600 -2.18949500 -2.02212000
H -0.12757600 -2.61089900 0.58006600
H -0.47517700 -4.31461100 0.21707900

4.1.2 Janus (**1**$_{out}$) Excited State

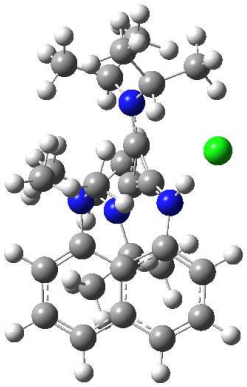

Figure S40. Computational model of Janus (**1**$_{out}$) excited state.

opt=calcfc freq=noraman td=singlets M062X/6-31+g(d,p) scrf=(smd,solvent=dichloromethane) geom=connectivity empiricaldispersion=gd3

Zero-point correction= 0.639011 (Hartree/Particle)
Thermal correction to Energy= 0.675055

Thermal correction to Enthalpy= 0.675999
Thermal correction to Gibbs Free Energy= 0.572820
Sum of electronic and zero-point Energies= -1731.503664
Sum of electronic and thermal Energies= -1731.467621
Sum of electronic and thermal Enthalpies= -1731.466677
Sum of electronic and thermal Free Energies= -1731.569855

N 0.44574300 1.53662000 -0.82160100
H -0.05027600 2.44306300 -0.92451000
N 0.29758200 -2.09103600 -0.71749400
N -2.77165700 0.03060200 -0.01708200
C -0.28738400 0.44017800 -0.63354400
C -0.36316900 -0.94268700 -0.58340700
C -1.49633800 -0.16235600 -0.33524500
C 1.84753600 1.53472600 -0.64604700
C 2.47580000 0.82608400 0.41403500
C 1.81454100 0.29871600 1.57750900
C 2.47844900 -0.66863600 2.42041200
H 1.93004700 -1.13402100 3.23184300
C 3.82367500 -0.90001100 2.26079100
H 4.33980500 -1.58489600 2.92697000
C 4.54025900 -0.23695100 1.24401000
H 5.60873400 -0.40712700 1.13932800
C 3.90127000 0.61334000 0.30756100
C 4.62852900 1.24229400 -0.72561700
H 5.70167600 1.08317200 -0.77767700
C 3.98803600 2.10629900 -1.64578000
H 4.57458900 2.63937000 -2.38785400
C 2.62001600 2.24866100 -1.61335000
H 2.09466900 2.87362300 -2.33071500
C -0.30130200 -0.05482900 2.79421700
C 0.26037600 2.17450700 1.98091800
H -0.22766200 -1.10607200 2.50593500
H -1.32773000 0.28656100 2.62270100
H -0.70421900 2.35877900 1.49485700
H 1.03212900 2.74779200 1.46985600
N 0.58019600 0.75548100 1.97497200
H -0.08216800 0.04920100 3.86642200
H 0.19453000 2.51510900 3.02434200
C -0.39503600 -3.38673900 -0.56615900
C -1.48843400 -3.57778600 -1.62097200
C -0.87776200 -3.55850800 0.87201600
H -1.05140500 -3.66514400 -2.61880900
H -0.02570500 -3.52731800 1.55871400
C 1.62078900 -2.04855000 -1.39180900
C 2.66462000 -2.84226600 -0.61539300
C 1.51666600 -2.51247000 -2.84301900
H 2.68369200 -2.53880700 0.43481300
C -3.64331100 -1.13808700 0.23500800
C -3.94562900 -1.34583800 1.72071200
C -4.91297700 -1.13529200 -0.61073600
H -3.03218000 -1.28072700 2.32001800
H -4.68169500 -1.01761800 -1.67320300
C -3.23045700 1.44566100 -0.04578100
C -4.10292000 1.81663800 1.14682800
C -3.88068000 1.82176300 -1.37736800
H -3.26063600 1.49137900 -2.21706300
Cl -1.03573600 4.30430900 -1.00374400
H -1.38416200 -4.52108800 0.98792700
H -1.57786100 -2.76924500 1.16220700
H -2.18958800 -2.73885700 -1.64145900
H -2.05413200 -4.49089600 -1.41263200
H 3.65173400 -2.65368600 -1.04876900
H 2.48035700 -3.92040600 -0.67055600
H 2.48294000 -2.37086400 -3.33652300
H 1.26170100 -3.57621200 -2.90187200
H 0.76294500 -1.93587000 -3.38804500
H -4.26318300 2.89892000 1.12562300
H 0.37563300 -4.14047300 -0.74624500
H 1.91346300 -0.99537400 -1.38257500
H -2.31140700 2.03578500 0.02644100
H -3.04475700 -1.98943500 -0.08973500
H -3.61769400 1.56211300 2.09401900
H -5.08333300 1.33324300 1.10842600
H -3.95889700 2.91166000 -1.43004000
H -4.88190200 1.39847700 -1.48599300
H -4.36959900 -2.34644900 1.85582800
H -4.66789200 -0.62116400 2.10272700
H -5.60496300 -0.34455200 -0.30878700
H -5.42212200 -2.09404600 -0.4726000

4.1.3 Janus (**1**$_{in}$) Ground State

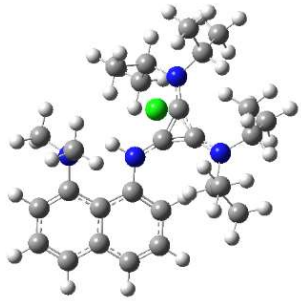

Figure S41. Computational model of Janus (**1**$_{in}$) ground state.

opt=calcfc freq=noraman M062X/6-31+g(d,p) scrf=(solvent=dichloromethane,smd) geom=connectivity empiricaldispersion=gd3

Zero-point correction= 0.641818 (Hartree/Particle)
Thermal correction to Energy= 0.67762
Thermal correction to Enthalpy= 0.678572
Thermal correction to Gibbs Free Energy= 0.574698
Sum of electronic and zero-point Energies= -1731.627151
Sum of electronic and thermal Energies= -1731.591341
Sum of electronic and thermal Enthalpies= -1731.590396
Sum of electronic and thermal Free Energies= -1731.694271

N 0.94518900 -0.34429400 -0.50976600
H 1.25889500 -1.29980600 -0.29227600
N -1.82842600 2.05276400 0.00155400
N -2.43234400 -1.57835700-0.75756000
C -0.36552100 -0.04742800-0.47329700
C -1.41602500 0.82185700 -0.26447000
C -1.65176900 -0.53021200-0.54656600
C 1.98117500 0.58237000 -0.67887100
C 3.32831600 0.21989800 -0.31706500
C 3.72161600 -1.05393400 0.22961500
C 5.05733100 -1.33263600 0.42723800
H 5.34959100 -2.29807000 0.82676600
C 6.06004800 -0.37680700 0.14823900
H 7.10121300 -0.62918000 0.32532100
C 5.71308200 0.86236000 -0.31960900
H 6.46951900 1.61554700 -0.52206500
C 4.35192000 1.18648500 -0.57265400
C 4.02734200 2.46278000 -1.10774400
H 4.82853500 3.17888300 -1.26561700
C 2.73316400 2.76277200 -1.44629800
H 2.48350700 3.72524100 -1.88351500
C 1.71502500 1.80686100 -1.25849500
H 0.70639600 2.02255000 -1.59589200
C 2.20242800 -1.75375000 1.94363200
C 3.09549500 -3.41554100 0.44179500
H 1.85313300 -0.72148200 2.02366000
H 2.98287900 -1.92521800 2.70084100
H 3.81357600 -3.74982300 1.20529500
H 3.52382900 -3.58169400 -0.54932300
N 2.71442100 -2.01323300 0.58942400
H 1.35935400 -2.42182200 2.14354200
H 2.19280900 -4.02520500 0.54386300
C -0.87111200 3.02962800 0.57136400
C -1.27569100 3.43673500 1.98583100
C -0.70344100 4.23776500 -0.34619300
H -1.39498500 2.55130100 2.61735200
H -0.44770900 3.93602400 -1.36644100
C -3.26392300 2.40083700 -0.06396400

C -3.81916700 2.09667200 -1.45383100
C -4.05160000 1.76486500 1.08515800
H -3.76196200 1.03226300 -1.70184000
C -1.79561900 -2.87782900-1.07019300
C -0.95003700 -2.78380400-2.33710200
C -0.99901700 -3.40855100 0.11900900
H -1.53777700 -2.38631000-3.17032900
H -1.62862700 -3.50123200 1.00820500
C -3.89213100 -1.52030200-0.54544700
C -4.30903400 -2.37960000 0.64488700
C -4.64520800 -1.87898000-1.82377300
H -4.32444800 -1.24710900-2.65786200
Cl -1.56157900 -0.41768800 2.96514400
H 0.09732400 4.87886100 0.03612000
H -1.61898300 4.83824500 -0.38622100
H -2.20879800 4.01017600 1.98842200
H -0.49330600 4.07220100 2.41226000
H -3.25933500 2.65065100 -2.21401800
H -4.86940600 2.39719600 -1.50836600
H -3.85567200 2.28784800 2.02497800
H -5.12645200 1.81254600 0.88223800
H -3.76085700 0.72269800 1.24225400
H -5.37998200 -2.25081800 0.83050400
H 0.08101900 2.49651000 0.63749100
H -3.29445000 3.48689800 0.06092400
H -4.10951000 -0.48003100-0.30440600
H -2.62525500 -3.56257900-1.26339700
H -3.75855800 -2.08275800 1.54337600
H -4.12801000 -3.44275400 0.45215500
H -5.71749600 -1.72601200-1.66783700
H -4.49685700 -2.92709900-2.10339600
H -0.58741200 -3.77866800-2.61224200
H -0.07621600 -2.13999600-2.18757100
H -0.16840800 -2.73908200 0.36876700
H -0.58203100 -4.39141700-0.121906

4.1.4 Janus (1_{out}) Ground State

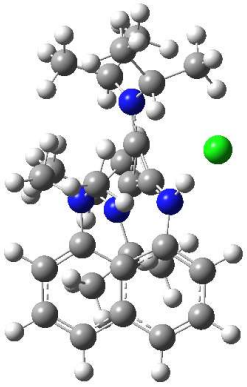

Figure S42. Computational model of Janus (**1_{out}**) ground state.

opt=calcfc freq=noraman M062X/6-31+g(d,p) scrf=(solvent=dichloromethane,smd) geom=connectivity empiricaldispersion=gd3

Zero-point correction= 0.642838 (Hartree/Particle)
Thermal correction to Energy= 0.678333
Thermal correction to Enthalpy= 0.679277
Thermal correction to Gibbs Free Energy= 0.576485

Sum of electronic and zero-point Energies= -1731.624828
Sum of electronic and thermal Energies= -1731.589333
Sum of electronic and thermal Enthalpies= -1731.588389
Sum of electronic and thermal Free Energies= -1731.691181

N 0.44574300 1.53662000 -0.82160100
H -0.05027600 2.44306300 -0.92451000
N 0.29758200 -2.09103600 -0.71749400
N -2.77165700 0.03060200 -0.01708200
C-0.28738400 0.44017800 -0.63354400
C -0.36316900 -0.94268700-0.58340700
C -1.49633800-0.16235600 -0.33524500
C 1.84753600 1.53472600 -0.64604700
C 2.47580000 0.82608400 0.41403500
C 1.81454100 0.29871600 1.57750900
C 2.47844900 -0.66863600 2.42041200
H 1.93004700 -1.13402100 3.23184300
C 3.82367500 -0.90001100 2.26079100
H 4.33980500 -1.58489600 2.92697000
C 4.54025900 -0.23695100 1.24401000
H 5.60873400 -0.40712700 1.13932800
C 3.90127000 0.61334000 0.30756100
C 4.62852900 1.24229400 -0.72561700
H 5.70167600 1.08317200 -0.77767700
C 3.98803600 2.10629900 -1.64578000
H 4.57458900 2.63937000 -2.38785400
C 2.62001600 2.24866100 -1.61335000
H 2.09466900 2.87362300 -2.33071500
C -0.30130200 -0.05482900 2.79421700
C 0.26037600 2.17450700 1.98091800
H -0.22766200 -1.10607200 2.50593500
H -1.32773000 0.28656100 2.62270100
H -0.70421900 2.35877900 1.49485700
H 1.03212900 2.74779200 1.46985600
N 0.58019600 0.75548100 1.97497200
H -0.08216800 0.04920100 3.86642200
H 0.19453000 2.51510900 3.02434200
C -0.39503600 -3.38673900-0.56615900
C -1.48843400-3.57778600-1.62097200
C -0.87776200-3.55850800 0.87201600
H -1.05140500-3.66514400 -2.61880900
H -0.02570500-3.52731800 1.55871400
C 1.62078900 -2.04855000 -1.39180900
C 2.66462000 -2.84226600 -0.61539300
C 1.51666600 -2.51247000 -2.84301900
H 2.68369200 -2.53880700 0.43481300
C -3.64331100 -1.13808700 0.23500800
C -3.94562900 -1.34583800 1.72071200
C -4.91297700 -1.13529200-0.61073600
H -3.03218000 -1.28072700 2.32001800
H -4.68169500 -1.01761800-1.67320300
C -3.23045700 1.44566100 -0.04578100
C -4.10292000 1.81663800 1.14682800
C -3.88068000 1.82176300 -1.37736800
H -3.26063600 1.49137900-2.21706300
Cl -1.035736004.30430900 -1.00374400
H -1.38416200 -4.52108800 0.98792700
H -1.57786100-2.76924500 1.16220700
H -2.18958800 -2.73885700-1.64145900
H -2.05413200 -4.49089600-1.41263200
H 3.65173400 -2.65368600 -1.04876900
H 2.48035700 -3.92040600 -0.67055600
H 2.48294000 -2.37086400 -3.33652300
H 1.26170100 -3.57621200 -2.90187200
H 0.76294500 -1.93587000 -3.3880450
H -4.26318300 2.89892000 1.12562300
H 0.37563300 -4.14047300 -0.74624500
H 1.91346300 -0.99537400 -1.38257500
H -2.31140700 2.03578500 0.02644100
H -3.04475700-1.98943500 -0.08973500
H -3.61769400 1.56211300 2.09401900
H -5.08333300 1.33324300 1.10842600
H-3.95889700 2.91166000 -1.43004000
H-4.88190200 1.39847700 -1.48599300
H -4.36959900 -2.34644900 1.85582800
H -4.66789200-0.62116400 2.10272700
H -5.60496300-0.34455200-0.30878700
H -5.42212200-2.09404600-0.47260000

5.0 Quantum Theory of Atoms in Molecules (QTAIM) Calculations

5.1 QTAIM Bond Critical Point Analysis of $\mathbf{1_{in}}$.

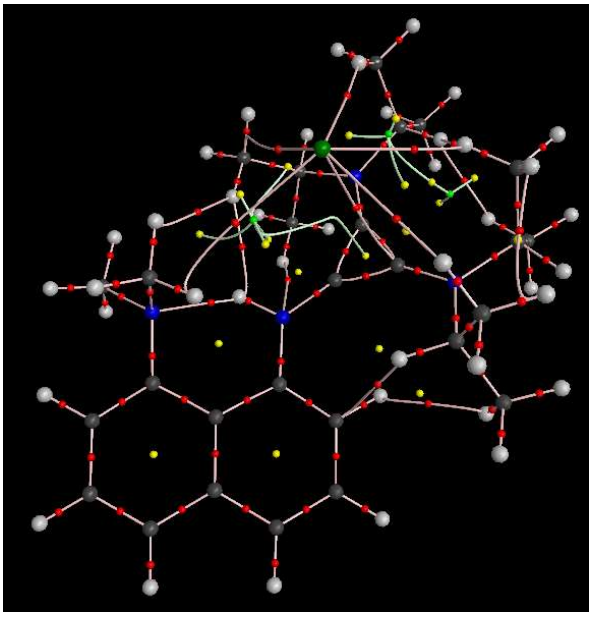

Figure S43. QTAIM Analysis of $\mathbf{1_{in}}^{\mathbf{GS}}$.

Property function to analyse: RHO, electron density

x: 3.32565146698685 y: -2.88575037108679 z: -0.00254732798924972

Density value:

0.0421366480822466

Gradient:

8.08904819992784e-016	-4.54671694558742e-016	6.12619541649037e-016

Hessian:

0.10465532749722	-0.101423806274017	0.0970889106376182
-0.101423806274017	0.00335043650712319	-0.0583295058619868
0.0970889106376182	-0.0583295058619868	-0.00402478342616081

Eigenvalues of Hessian:

-0.061247834264343	-0.0584694978528425	0.223698312695368

Eigenvectors of Hessian:

-0.609581718777869	-0.215959483066949	0.762739555684165
-0.291408940286465	-0.833759815711832	-0.468962044546563
0.737218392101649	-0.508139814792768	0.445312217404186

Rho, Charge Density:	0.0421366480822466
L, Laplacian of Rho:	-0.0259952451445456
KEG, Lagrangian Kinetic Energy:	0.0290916567454818
KEK, Hamiltonian Kinetic Energy:	0.0030964116009362
VIR, Virial Field Function:	0.0321880683464179

Figure S44. Bond critical point (BCP) information for N11 – H29 in $\mathbf{1_{in}}^{\mathbf{GS}}$.

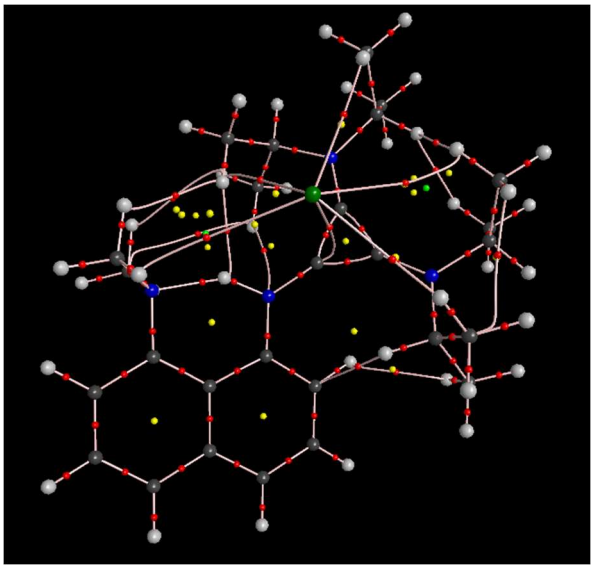

Figure S45. QTAIM Analysis of $\mathbf{1}_{\mathbf{in}}^{\mathbf{S1}}$.

Property function to analyse: RHO, electron density

x: 3.27532662779877 y: -2.73940057472378 z: 0.156563308769163

Density value:

0.0723634978214055

Gradient:

-2.64486884813103e-016	1.2172879891581e-016	-1.54883974650891e-016

Hessian:

0.186700340854436	-0.221772129759546	0.119153895410737
-0.221772129759546	0.0150129874183594	-0.0816102931580208
0.119153895410737	-0.0816102931580208	-0.0946056720594277

Eigenvalues of Hessian:

-0.138333820023336	-0.136949410261548	0.382390886498252

Eigenvectors of Hessian:

0.250764304624179	0.560138953855462	0.789532529982179
-0.146590069590516	0.828159085299657	-0.540984178080175
-0.956884849406552	0.0199218927148946	0.289783545369395

Rho, Charge Density:	0.0723634978214055
L, Laplacian of Rho:	-0.0267769140533421
KEG, Lagrangian Kinetic Energy:	0.04445680848088
KEK, Hamiltonian Kinetic Energy:	0.017679894427538
VIR, Virial Field Function:	0.062136702908418

Figure S46. Bond critical point (BCP) information for N11 – H29 in $\mathbf{1}_{\mathbf{in}}^{\mathbf{S1}}$.

5.2 QTAIM Bond Critical Point Analysis of $\mathbf{1}_{\mathbf{out}}$.

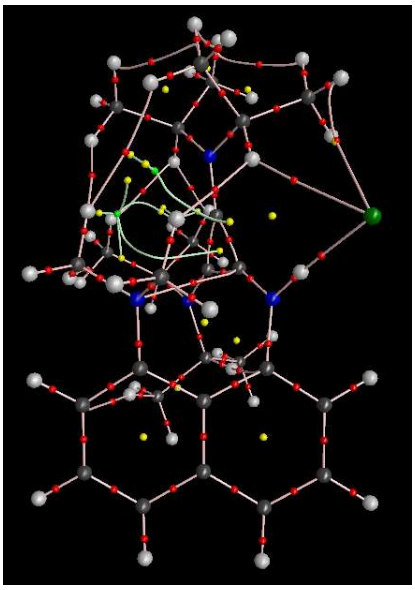

Figure S47. QTAIM analysis of $\mathbf{1}_{\mathbf{out}}^{GS}$.

Property function to analyse: RHO, electron density

x: 0.46650617396035 y: -5.62985191548845 z: -1.87177575445943

Density value:

0.0327988263257947

Gradient:

3.76602230354491e-017	-9.98402764186768e-017	5.51354788842607e-017

Hessian:

-0.0145283925341065	-0.062506079009154	-0.00628703310863867
-0.062506079009154	0.116692942943778	0.0160198477249172
-0.00628703310863867	0.0160198477249172	-0.0372705432262916

Eigenvalues of Hessian:

-0.0395563398355356	-0.038890449290894	0.14334079630981

Eigenvectors of Hessian:

-0.908486026429131	-0.194806696162954	-0.369734351816386
-0.381031570657606	0.0227024339477214	0.924283258344025
0.171662698176415	-0.980578885466602	0.0948523454210247

Rho, Charge Density:	0.0327988263257947
L, Laplacian of Rho:	-0.016223501795845
KEG, Lagrangian Kinetic Energy:	0.0189580225059016
KEK, Hamiltonian Kinetic Energy:	0.00273452071005669
VIR, Virial Field Function:	0.0216925432159583

Figure S48. Bond critical point (BCP) information for Cl30 – H29 in $\mathbf{1}_{\mathbf{out}}^{GS}$.

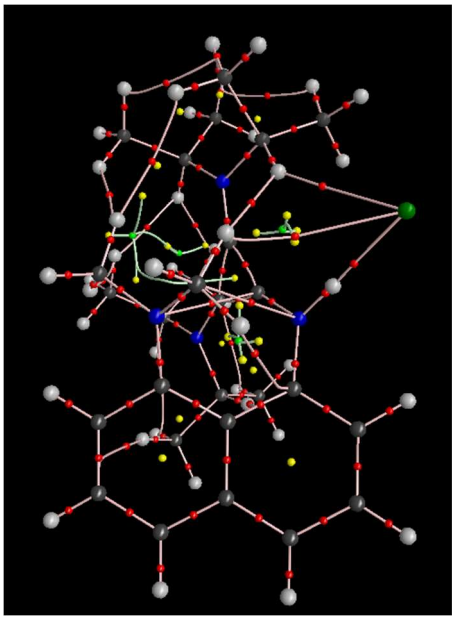

Figure S49. QTAIM analysis of $\mathbf{1}_{out}^{S1}$.

Property function to analyse: RHO, electron density

x: -0.683767474217639 y: 5.70840447539066 z: -1.78135296616259

Density value:

0.0323813725967869

Gradient:

3.70511878175275e-016	-4.88799122669387e-016	-1.32544959665994e-016

Hessian:

0.000871699468157326	-0.0746039887008635	0.00355282344962048
-0.0746039887008635	0.101623830249461	-0.00693928118559293
0.00355282344962048	-0.00693928118559293	-0.0378639965737739

Eigenvalues of Hessian:

-0.0387954784473386	-0.0381787771757639	0.141605788766947

Eigenvectors of Hessian:

0.861885446211133	0.193386374608107	0.468780532579339
0.467610667708268	0.0545744443972609	-0.882248204001662
0.196198218786165	-0.979603664823005	0.0433926123951204

Rho, Charge Density:	0.0323813725967869
L, Laplacian of Rho:	-0.016157883285961
KEG, Lagrangian Kinetic Energy:	0.0187837711287758
KEK, Hamiltonian Kinetic Energy:	0.00262588784281483
VIR, Virial Field Function:	0.0214096589715907

Figure S50. Bond critical point (BCP) information for Cl30 – H29 in $\mathbf{1}_{out}^{S1}$.

6.0 Natural Bond Order (NBO) Analysis

Table S2. NBO analysis of the N_{11} lone-pair to the naphthalene ring (C_8).

Geometry	Donor NBO	Acceptor NBO	kcal mol^{-1}
1_{in} (GS)	N_{11} (LP)	C_7-C_8 (BD*)	6.50
1_{in} (S1)	N_{11} (LP)	C_7-C_8 (BD*)	7.62
1_{out} (GS)	N_{11} (LP)	C_7-C_8 (BD*)	18.87
1_{out} (S1)	N_{11} (LP)	C_7-C_8 (BD*)	38.90

7.0 References

[1] Dawson, W. R.; Windsor, M. W. Fluorescence yields of aromatic compounds. *J. Chem. Phys.* **1968**, *72*, 3251-3260.

[2] Brouwer, A. M. Standards for photoluminescence quantum yield measurements in solution. *Pure Appl. Chem.* **2011**, *83*, 2213-2228.